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(54) **SYNTHESIS OF VINYL POLYMERS BY CONTROLLED RADICAL POLYMERIZATION**
SYNTHESE VON VINYLPOLYMEREN DURCH KONTROLLIERTE RADIKALPOLYMERISATION
SYNTHESE DE POLYMERES VINyliQUES PAR POLYMERISATION RADICALAIRE CONTROLEE

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21.01.2004 Bulletin 2004/04</p> <p>(73) Proprietor: PPG Industries Ohio, Inc.
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FR-A- 2 653 433</p> <ul style="list-style-type: none">• PATENT ABSTRACTS OF JAPAN vol. 016, no. 556
(C-1007), 26 November 1992 (1992-11-26) & JP 04
213307 A (NIPPON STEEL CHEM CO LTD;
OTHERS: 01), 4 August 1992 (1992-08-04)• PATENT ABSTRACTS OF JAPAN vol. 011, no. 075
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(1986-10-17) |
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Description**FIELD OF THE INVENTION**

[0001] The present invention is directed to a method of controlled radical polymerization of vinyl monomers. Specifically, the invention is directed to a method of controlled polymerization of vinyl monomers using an iniferter initiator, which is capable of forming a carbon centered radical.

BACKGROUND OF THE INVENTION

[0002] A wide variety of radically polymerizable monomers, such as methacrylic and acrylic monomers, is commercially available and can confer a wide range of properties to a polymer or copolymer (hereinafter, collectively referred to as (co)polymer). The use of conventional free radical (co)polymerization methods to synthesize (co)polymers provides little control over molecular weight, molecular weight distribution and, in particular, (co)polymer chain structure.

[0003] In order to overcome this problem, polymerization methods based ionic methods (anionic and cationic polymerization) were developed that would enable the artisan a degree of control over the placement of monomers along a growing polymer chain. These methods are limited, however, to a relatively narrow class of monomer and polymer types.

[0004] A further development provides a method of free radical polymerization, in which a "living" polymer containing a radically transferable atom or group is employed to enable a degree of control over (co)polymer composition and architecture. These methods, referred to collectively as atom or group radical transfer polymerization (ATRP), are described in, for example, United States Patent Nos. 5,807,937, 5,789,487 and 5,763,548 to Matyjaszewski et al. The ATRP method is described as providing highly uniform products having controlled structure (i.e., controllable topology, composition, etc.).

[0005] However, ATRP type processes require the use of halogenated hydrocarbon initiators and transition metal catalysts, which cause safety and material compatibility concerns when implemented at production scale. Further, although more versatile than ionic polymerization methods, a number of functional monomers, for example carboxylic acid functional monomers, cannot be polymerized directly using ATRP methodologies.

[0006] A further technique that has been explored to provide control over a radical polymerization process is those processes utilizing iniferter initiators. Iniferter initiators contain a chemical bond that will break under appropriate thermal or photolytic conditions, forming two carbon centered radicals. The radicals are capable of polymerizing monomers and the polymerization step competes with radical recombination. Functional groups that have found use in iniferter initiators include thiuram disulfides, dithiocarbamate disulfides and ethylene derivatives that contain at least four stabilizing groups.

[0007] Thiuram iniferter initiators are disclosed in, for example, U.S. Patent No. 6,169,147 to Kroeze et al.; Lokaj et al., *Journal of Applied Polymer Science*, 67, 755-762 (1998); Kroeze et al., *Macromolecules*, 28, 6650-6656 (1995); Nair et al., *J. Macromol. Sci.-Chem.*, A27(6), 791-806 (1990); and Nair et al., *Polymer*, 29, 1909-1917 (1988). Thiuram disulfide iniferter initiated polymerizations are able to produce block copolymers, but typically with limited control and wide molecular weight distributions.

[0008] Dithiocarbamate disulfide iniferter initiators are disclosed in, for example, U.S. Patent Nos. 5,866,047 to Nagino et al., 5,658,986 to Clouet and 5,489,654 to Clouet; Suwier et al., *Journal of Polymer Science: Part A: Polymer Chemistry*, 38, 3558-3568 (2000); and Nair et al., *Macromolecules*, 23, 1361-1369 (1990). Dithiocarbamate disulfide iniferter initiated polymerizations are able to produce block copolymers, but typically with limited control and wide molecular weight distributions.

[0009] Various multisubstituted ethylene derivatives have been disclosed as iniferter initiators. For example, U.S. Patent No. 5,866,047 to Nagino et al., Chen et al., *European Polymer Journal*, 36, 1547-1554 (2000), Tharanikkarusa et al., *Journal of Applied Polymer Science*, 66, 1551-1560 (1997); and Tharanikkarusa et al., *J.M.S.-Pure Appl. Chem.*, A33(4), 417-437 (1996) disclose derivatives of 1,1,2,2-tetraphenyl-1,2-ethanediol as iniferter initiators. The use of phenylazotriphenyl methane as an iniferter initiator is disclosed by Otsu et al., *Polymer Bulletin*, 16, 277-284 (1996). Various 1,2-dicyano-1,2-diphenylethane derivatives are described as iniferter initiators by Qin et al., *Macromolecules*, 33, 6987-6992 (2000); Qin et al., *Journal of Polymer Science: Part A: Polymer Chemistry*, 38, 2115-2120 (2000); Qin et al., *Polymer*, 41, 7347-7353 (2000); Qin et al., *Journal of Polymer Science: Part A: Polymer Chemistry*, 37, 4610-4615 (1999); Tharanikkarusa et al., *European Polymer Journal*, 33, 1779-1789 (1997); Tazaki et al., *Polymer Bulletin*, 17, 127-134 (1987); and Otsu et al., *Polymer Bulletin*, 17, 323-330 (1987). The multisubstituted ethylene derivative iniferter initiated polymerizations are all able to produce block copolymers, but typically also demonstrate limited control of the polymerization process and the resulting polymers had wide molecular weight distributions.

[0010] All of the cited iniferter technology utilized either disulfide groups or ethylene derivatives with multiple radical stabilizing groups, such as phenyl and cyano, to effect a somewhat controlled polymerization process. In the case of disulfide iniferters, the sulfide and dithiocarbamate groups are prone to side reactions and early termination reactions. The multi-phenyl substituted ethylene iniferters are similarly prone to side reactions and early termination reactions.

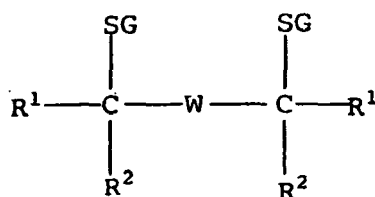
These problems lead to poor control of the polymerization process and a wide, bimodal or multimodal molecular weight distribution.

[0011] There remains a need for a method of controlled polymerization, which is capable of polymerizing a wide variety of functional monomers. The controlled polymerization method should also provide for copolymer composition and architecture control as well as providing for control over polymer molecular weight and molecular weight distribution.

SUMMARY OF THE INVENTION

[0012] In accordance with the present invention, there is provided a controlled free radical polymerization process, which includes the steps of:

(a) adding a compound capable of forming a carbon centered radical, which is able to initiate free radical polymerization, having the general structure:



wherein R¹ is selected from the group consisting of C₁-C₂₀ alkyl, cyclic, heterocyclic, alkynol, or aryl; R² is selected from the group consisting of H and C₁-C₄ alkyl; SG is a radical stabilizing group; and W is selected from the group consisting of a -C-C- bond and a group that can decompose to form two residues containing carbon centered radicals; to a solvent, forming a solution, which is substantially free of oxygen;

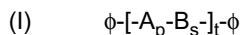
(b) heating the solution to a temperature 20°C to 250°C;

(c) adding a first monomer composition comprising one or more ethylenically unsaturated monomers to the solution containing the carbon centered radical residues; and

(d) polymerizing the first monomer composition to form a quasi-living polymer;

optionally adding a second, third, fourth, etc. monomer composition comprising one or more ethylenically unsaturated monomers, which is different than the first monomer composition, to the quasi-living polymer solution; and polymerizing the second monomer composition.

[0013] The present invention is further directed to a non-random copolymer of general formula I:



where A and B are different compositions of ethylenically unsaturated monomers; p is an integer from 1 to 1,000; s is an integer from 1 to 1,000; t is an integer from 1 to 100; and ϕ is a residue from a carbon centered radical capable of initiating free radical polymerization.

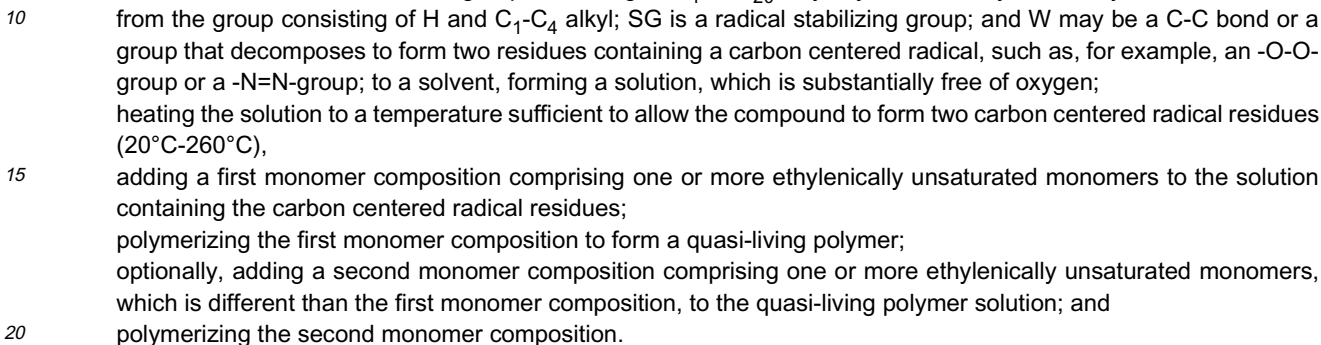
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0014] The terms (meth)acrylic and (meth)acrylate are meant to include both acrylic and methacrylic acid derivatives, such as the corresponding alkyl esters often referred to as acrylates and (meth)acrylates, which the term (meth)acrylate is meant to encompass.

[0015] Unless otherwise noted, the term copolymer is meant to include polymers containing more than one monomer in all forms, i.e., random, alternating, block, gradient, etc.

[0016] The controlled free radical polymerization process of the present invention can generally be described as including the steps of:

adding a compound capable of forming a carbon centered radical, which is able to initiate free radical polymerization (an iniferter), of general structure II:

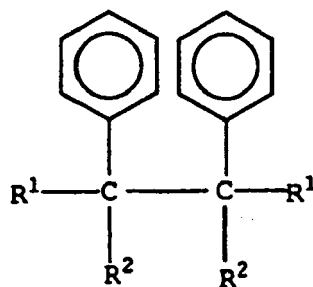


25 **[0018]** The radical stabilizing group, SG, of the iniferter of the present invention can be any functional group that is capable of stabilizing a free radical at the adjacent carbon atom. The most effective radical stabilizing groups are able to delocalize the radical through various resonance structures. Examples of radical stabilizing groups that can be used as part of the present invention include, but are not limited to nitrile, ester, amide, carboxyl, allyl, nitro, aryl and halide.

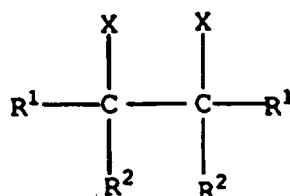
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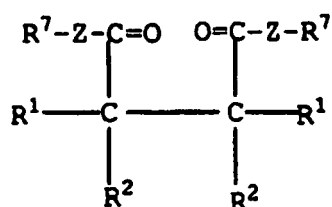
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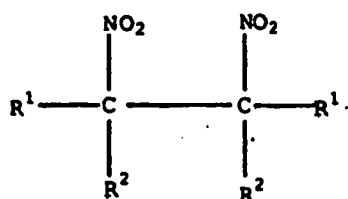
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(VII)



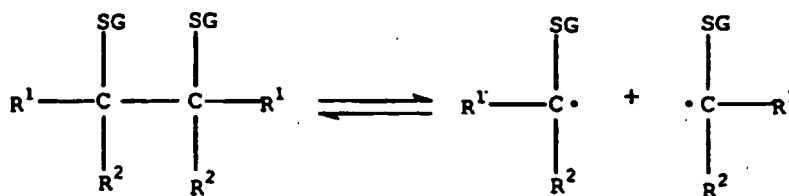
(VIII)



where R^1 and R^2 are independently selected from H, $\text{C}_1\text{-C}_{20}$ alkyl, cyclic, heterocyclic and alkynol, R^7 is selected from H, $\text{C}_1\text{-C}_{20}$ alkyl, cyclic, heterocyclic, alkynol, and aryl; Z is O or NH; and X is a halogen.

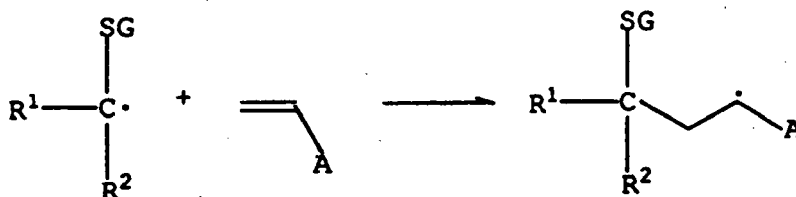
[0020] In general, the iniferter compound capable of forming a carbon centered radical breaks down, when exposed to a sufficient temperature or light, to form two carbon centered radical residues as described in Scheme I:

Scheme I



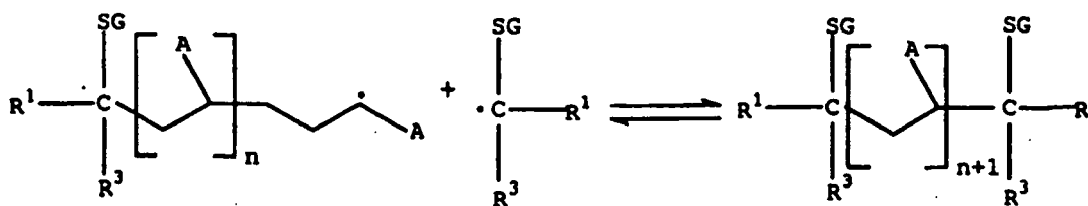
[0021] Surprisingly, this is accomplished with an iniferter residue containing only one stabilizing group for the free radical. Each carbon centered radical residue is capable of then initiating polymerization as shown in Scheme II:

Scheme II



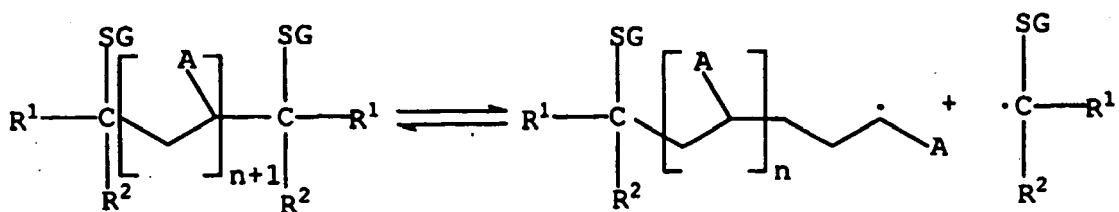
[0022] The polymer may grow through conventional free radical addition polymerization, or recombine with a carbon centered radical residue as shown in Scheme III:

Scheme III



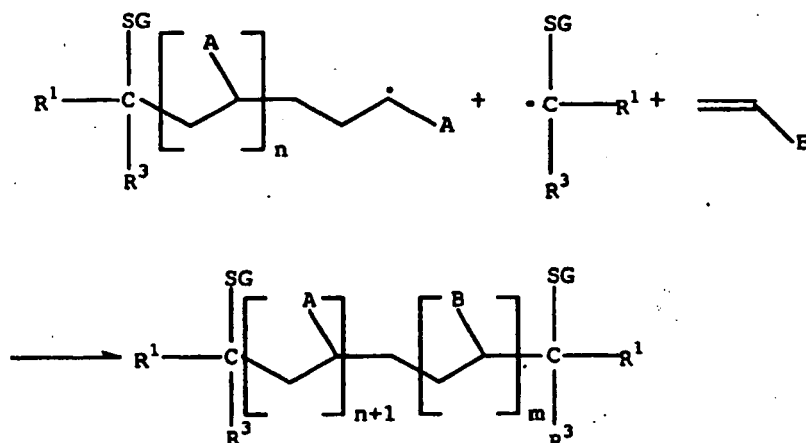
[0023] The terminal carbon centered radical residue is able, when exposed to a sufficient temperature or light, to break down and reform a carbon centered free radical residue, a quasi-living free radical polymer, as shown in Scheme IV:

Scheme IV



[0024] When a second monomer is added to the "quasi-living" polymer, a block copolymer is achieved as depicted in Scheme V.

Scheme V



[0025] With regard to Schemes I-V, A and B represent functional groups of different polymerizable ethylenically unsaturated monomers and n and m are integers representing the block lengths of each monomer composition represented by A and B, respectfully. R¹, R² and SG are as described above.

[0026] In the present invention, it has been found that certain compounds capable of forming carbon centered radicals are capable of acting as iniferter initiators providing a quasi-living polymer, which can be used to control the polymerization process. As opposed to prior art iniferters, the iniferters of the present invention contain only one stabilizing group in the free radical containing residue. This effect is obtained by regulating the temperature and monomer addition of the polymerization process. The method of the present invention does not require the presence of transition metals or potential corrosive halides.

[0027] The iniferter compound of the present invention can be a bis tertiary alkyl compound, which is added directly to a solvent. An azobis tertiary alkyl compound can also be used and is added to a solvent, heated to decompose to form free radical containing residues that then recombine and are capable of acting as iniferters, breaking down to reform free radical containing residues.

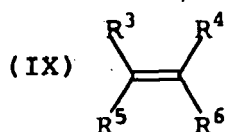
[0028] Examples of suitable azobis tertiary alkyl compounds include, but are not limited to, 4,4'-azobis(4-cyanovaleric acid), 1,1'-azobiscyclohexanecarbonitrile, 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylpropionamide) dihydrochloride, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(propionitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(valeronitrile), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 4,4'-azobis(4-cyanopentanoic acid), 2,2'-azobis(N,N'-dimethyleisobutyramidine), 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleisobutyramidine) dihydrochloride, and 2-(carbamoilazo)-isobutyronitrile.

[0029] Preferred azobis tertiary alkyl compounds include 2,2'-azobis(2-methyl-butyronitrile), dimethyl 2,2'-azobisisobutyrate and 4,4'-azobis(4-cyanopentanoic acid)

[0030] Examples of suitable bis tertiary alkyl compounds include, but are not limited to, 4,5 dicyano-4,5 dimethyl suberic acid, 1,1'-dicyanodicyclohexyl, 2,3-dicyano-2,3-dimethylbutane, 2, 2, 3, 3-tetramethyl-1,4-diamidinylbutane dihydrochloride, 2, 2, 3, 3-tetramethyl-N,N'-dihydroxyethyl succinamide, and 2, 2, 3, 3-tetramethyl-N,N'-tetramethylene succinamide.

[0031] In the method of the present invention, the iniferter is decomposed at a temperature that will accomplish the decomposition but minimize the occurrence of unwanted or unanticipated side and competing reactions. The method can be performed at any temperature that accomplishes this aim. The controlled polymerization process of the present invention is performed at from 20°C to 250°C, preferably from 50°C to 200°C, and more preferably from 60°C to 150°C.

[0032] In the present invention any ethylenically unsaturated monomer can be used. The ethylenically unsaturated monomers can be described by general formula IX:



wherein R³, R⁴ and R⁶ are independently selected from the group consisting of H, halogen, CN, CF₃, straight or branched

alkyl of 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms), aryl, unsaturated straight or branched alkenyl or alkynyl of 2 to 10 carbon atoms (preferably from 2 to 6 carbon atoms, more preferably from 2 to 4 carbon atoms), unsaturated straight or branched alkenyl of 2 to 6 carbon atoms (preferably vinyl) substituted (preferably at the α -position) with a halogen (preferably chlorine), C₃-C₈ cycloalkyl, heterocyclyl, phenyl, which may optionally have from 1-5 substituents on the phenyl ring, C(=Y)R⁹, C(=Y)NR¹⁰R¹¹, YCR¹⁰R¹¹R¹² and YC(=Y)R¹², where Y may be NR¹² or O (preferably O), R⁹ is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy, R¹⁰ and R¹¹ are independently H or alkyl of from 1 to 20 carbon atoms, or R¹⁰ and R¹¹ may be joined together to form an alkylene group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring, and R¹² is H, straight or branched C₁-C₂₀, alkyl and aryl; R⁵ is selected from the group consisting of H, halogen, C₁-C₆ alkyl, CN, COOR⁸, wherein R⁸ is selected from the group consisting of H, an alkali metal, a C₁-C₆ alkyl group and aryl.

[0033] Specific examples of vinyl monomers that may be polymerized by the method of the present invention include vinyl monomers, allylic monomers, olefins, (meth)acrylic acid, (meth)acrylates, (meth)acrylamide, N- and N,N-disubstituted (meth)acrylamides, vinyl aromatic monomers, vinyl halides vinyl esters of carboxylic acids and mixtures thereof. More specific examples of suitable monomers include, without limitation, C₁-C₂₀ alkyl (meth)acrylates (including linear or branched alkyls and cycloalkyls) which include, but are not limited to, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, isobornyl (meth)acrylate, cyclohexyl (meth)acrylate, 3,3,5-trimethylcyclohexyl (meth)acrylate and isocane (meth)acrylate: oxirane functional (meth)acrylates which include, but are not limited to, glycidyl (meth)acrylate, 3,4-epoxycyclohexylmethyl(meth)acrylate, and 2-(3,4-epoxycyclohexyl) ethyl(meth)acrylate; hydroxy alkyl (meth)acrylates having from 2 to 4 carbon atoms in the alkyl group which include, but are not limited to, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate and hydroxybutyl (meth)acrylate. The residues may each independently be residues of monomers having more than one (meth)acryloyl group, such as (meth)acrylic anhydride, diethyleneglycol bis(meth)acrylate, 4,4'-isopropylidenediphenol bis(meth)acrylate (bisphenol A di(meth)acrylate), alkoxyated 4,4'-isopropylidenediphenol bis(meth)acrylate, trimethylolpropane tris(meth)acrylate and alkoxyated trimethylolpropane tris(meth)acrylate.

[0034] In the context of the present application, the terms "alkyl", "alkenyl" and "alkynyl" refer to straight-chain or branched groups. Furthermore, in the present application, "aryl" refers to phenyl, naphthyl, phenanthryl, phenalenyl, anthracenyl, triphenylenyl, fluoranthenyl, pyrenyl, pentacenyl, chrysenyl, naphthacenyl, hexaphenyl, picenyl and perylenyl (preferably phenyl and naphthyl), in which each hydrogen atom may be replaced with alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms and more preferably methyl), alkyl of from 1 to 20 carbon atoms (preferably from 1 to 6 carbon atoms and more preferably methyl) in which each of the hydrogen atoms is independently replaced by a halide (preferably a fluoride or a chloride), alkenyl of from 2 to 20 carbon atoms, alkynyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 6 carbon atoms, alkylthio of from 1 to 6 carbon atoms, C₃-C₈ cycloalkyl, phenyl, halogen, NH₂, C₁-C₆ -alkylamino, C₁-C₆ -dialkylamino, and phenyl which may be substituted with from 1 to 5 halogen atoms and/or C₁-C₄, alkyl groups. (This definition of "aryl" also applies to the aryl groups in "aryloxy" and "aralkyl".) Thus, phenyl may be substituted from 1 to 5 times and naphthyl may be substituted from 1 to 7 times (preferably any aryl group, if substituted, is substituted from 1 to 3 times) with one of the above substituents. More preferably, "aryl" refers to phenyl, naphthyl, phenyl substituted from 1 to 5 times with fluorine or chlorine, and phenyl substituted from 1 to 3 times with a substituent selected from the group consisting of alkyl of from 1 to 6 carbon atoms, alkoxy of from 1 to 4 carbon atoms and phenyl. Most preferably, "aryl" refers to phenyl and tolyl.

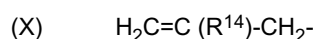
[0035] Specific examples of vinyl aromatic monomers that may be used to prepare the (co)polymer include, but are not limited to, styrene, p-chloromethyl styrene, divinyl benzene, vinyl naphthalene and divinyl naphthalene. Vinyl halides that may be used to prepare the graft (co)polymer include, but are not limited to, vinyl chloride, p-chloromethylstyrene, vinyl chloroacetate and vinylidene fluoride. Vinyl esters of carboxylic acids that may be used to prepare the graft (co)polymer include, but are not limited to, vinyl acetate, vinyl butyrate, vinyl 3,4-dimethoxybenzoate and vinyl benzoate.

[0036] In the context of the present invention, "heterocyclyl" refers to pyridyl, furyl, pyrrolyl, thienyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, pyranyl, indolyl, isoindolyl, indazolyl, benzofuryl, isobenzofuryl, benzothienyl, isobenzothienyl, chromenyl, xanthenyl, purinyl, pteridinyl, quinolyl, isoquinolyl, phthalazinyl, quinazolinyl, quinoxalinyl, naphthyridinyl, phenoxathiinyl, carbazolyl, cinnolinyl, phenanthridinyl, acridinyl, 1,10-phenanthrolinyl, phenazinyl, phenoxazinyl, phenothiazinyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, and hydrogenated forms thereof known to those in the art. Preferred heterocyclyl groups include pyridyl, furyl, pyrrolyl, thienyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, pyranyl and indolyl, the most preferred heterocyclyl group being pyridyl. Accordingly, suitable vinyl heterocyclyls to be used as a monomer in the present invention include 2-vinyl pyridine, 4-vinyl pyridine, 2-vinyl pyrrole, 3-vinyl pyrrole, 2-vinyl oxazole, 4-vinyl oxazole, 5-vinyl oxazole, 2-vinyl thiazole, 4-vinyl thiazole, 5-vinyl thiazole, 2-vinyl imidazole, 4-vinyl imidazole, 3-vinyl pyrazole, 4-vinyl pyrazole, 3-vinyl pyridazine, 4-vinyl pyridazine, 3-vinyl isoxazole, 3-vinyl isothiazoles, 2-vinyl pyrimidine, 4-vinyl pyrimidine, 5-vinyl pyrimidine, and any vinyl pyrazine, the most preferred being 2-vinyl, pyridine. The vinyl heterocyclyls mentioned above may bear one or more (preferably 1 or 2) C₁-C₆ alkyl or alkoxy

groups, cyano groups, ester groups or halogen atoms, either on the vinyl group or the heterocyclyl group, but preferably on the heterocyclyl group. Further, those vinyl heterocyclyls which, when unsubstituted, contain an N-H group may be protected at that position with a conventional blocking or protecting group, such as a C₁-C₆ alkyl group, a tris-C₁-C₆ alkylsilyl group, an acyl group of the formula R¹³ CO (where R¹³ is alkyl of from 1 to 20 carbon atoms, in which each of the hydrogen atoms may be independently replaced by halide, preferably fluoride or chloride), alkenyl of from 2 to 20 carbon atoms (preferably vinyl), alkynyl of from 2 to 10 carbon atoms (preferably acetylenyl), phenyl which may be substituted with from 1 to 5 halogen atoms or alkyl groups of from 1 to 4 carbon atoms, or aralkyl (aryl-substituted alkyl, in which the aryl group is phenyl or substituted phenyl and the alkyl group is from 1 to 6 carbon atoms), etc. (This definition of "heterocyclyl" also applies to the heterocyclyl groups in "heterocyclyloxy" and "heterocyclic ring.")

[0037] More specifically, preferred monomers include, but are not limited to, styrene, p-chloromethylstyrene, vinyl chloroacetate, acrylate and methacrylate esters of C₁-C₂₀ alcohols, isobutene, 2-(2-bromopropionyloxy) ethyl acrylate, acrylonitrile, and methacrylonitrile.

[0038] As used herein, by "allylic" and "allylic monomer(s)" is meant monomers or stabilizing groups (SG) containing substituted and/or unsubstituted allylic functionality, i.e., one or more radicals represented by the following general formula X,



wherein R¹⁴ is hydrogen, halogen or a C₁-C₄ alkyl group. Most commonly, R¹⁴ is hydrogen or methyl and, consequently, general formula X represents the unsubstituted (meth)allyl radical. Examples of allylic monomers include, but are not limited to, (meth)allyl ethers, such as methyl (meth)allyl ether and (meth)allyl glycidyl ether; allyl esters of carboxylic acids, such as (meth)allyl acetate, (meth)allyl butyrate, (meth)allyl 3,4-dimethoxybenzoate and (meth)allyl benzoate.

[0039] Other ethylenically unsaturated radically polymerizable monomers that may be used to prepare the (co)polymer include, but are not limited to, cyclic anhydrides, e.g., maleic anhydride, 1-cyclopentene-1,2-dicarboxylic anhydride and itaconic anhydride; esters of acids that are unsaturated but do not have α,β-ethylenic unsaturation, e.g., methyl ester of undecylenic acid; diesters of ethylenically unsaturated dibasic acids, e.g., di(C₁-C₄ alkyl)ethyl maleates; maleimide and N-substituted maleimides.

[0040] In one embodiment of the present invention, the monomer includes a hydrophobic residue of a monomer selected from an oxirane functional monomer reacted with a carboxylic acid selected from the group consisting of aromatic carboxylic acids, polycyclic aromatic carboxylic acids, aliphatic carboxylic acids having from 6 to 20 carbon atoms and mixtures thereof; C₆-C₂₀ alkyl (meth)acrylates, e.g., including those as previously recited herein; aromatic (meth)acrylates, e.g., phenyl (meth)acrylate, p-nitrophenyl (meth)acrylate and benzyl (meth)acrylate; polycyclic aromatic (meth)acrylates, e.g., 2-naphthyl (meth)acrylate; vinyl esters of carboxylic acids, e.g., hexanoic acid vinyl ester and decanoic acid vinyl ester; N,N-di(C₁-C₈ alkyl) (meth)acrylamides; maleimide; N-(C₁-C₂₀ alkyl) maleimides; N-(C₃-C₈ cycloalkyl) maleimides; N-(aryl) maleimides; and mixtures thereof. Examples of N-substituted maleimides include, but are not limited to, N-(C₁-C₂₀ linear or branched alkyl) maleimides, e.g., N-methyl maleimide, N-tertiary-butyl maleimide, N-octyl maleimide and N-icosane maleimide; N-(C₃-C₈ cycloalkyl) maleimides, e.g., N-cyclohexyl maleimide; and N-(aryl) maleimides, e.g., N-phenyl maleimide, N-(C₁-C₉ linear or branched alkyl substituted phenyl) maleimide, N-benzyl maleimide and N-(C₁-C₉, linear or branched alkyl substituted benzyl) maleimide.

[0041] The oxirane functional monomer or its residue that is reacted with a carboxylic acid may be selected from, for example, glycidyl (meth)acrylate, 3,4-epoxycyclohexylmethyl(meth)acrylate, 2-(3,4-epoxycyclohexyl) ethyl(meth)acrylate, allyl glycidyl ether and mixtures thereof. Examples of carboxylic acids that may be reacted with the oxirane functional monomer or its residue include, but are not limited to, para-nitrobenzoic acid, hexanoic acid, 2-ethyl hexanoic acid, decanoic acid, undecanoic acid and mixtures thereof.

[0042] The monomer containing at least one polar group may be present in an amount of 5 to 100 wt % by weight based on the total amount of monomers. A preferred amount of the monomer containing at least one polar group is 10 to 100 wt %; the most preferred amount is 20 to 100 wt % based on the total amount of monomers. This is particularly important in the case of acrylonitrile because an amount of at least 20 wt % assures solvent resistance properties of the resulting (co)polymer A.

[0043] A particular advantage of the controlled radical polymerization of the present invention is that carboxylic acid containing monomers can be polymerized directly. In other controlled polymerization methods (ATRP, anionic, etc.) the carboxylic acid functionality on a monomer must be blocked prior to polymerization and then unblocked after polymerization. The present method does not require blocking of such monomers.

[0044] Examples of carboxylic acid functional monomers include, but are not limited to, (meth)acrylic acid, maleic acid, fumaric acid and undecylenic acid. The monomer may be a residue of a precursor of a carboxylic acid functional monomer that is converted to a carboxylic acid residue after completion of the controlled radical polymerization, e.g., maleic anhydride, di(C₁-C₄ alkyl) maleates and C₁-C₄ alkyl (meth)acrylates. For example, residues of maleic anhydride can be converted to diacid residues, ester/acid residues or amide/acid residues by art-recognized reactions with water,

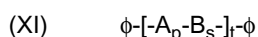
alcohols or primary amines, respectively. Residues of C₁-C₄ alkyl (meth)acrylates, such as t-butyl (meth)acrylate, can be converted to (meth)acrylic acid residues by art-recognized ester hydrolyzation methods, which typically involve the concurrent removal of an alcohol, such as t-butanol by vacuum distillation. Salts of carboxylic acid functional monomers include, for example, salts of (meth)acrylic acid and primary, secondary or tertiary amines, such as, butyl amine, dimethyl amine and triethyl amine.

[0045] Amine functional monomers include, for example, amino(C₂-C₄ alkyl) (meth)acrylates, e.g., 2-aminoethyl (meth)acrylate, 3-aminopropyl (meth)acrylate and 4-aminobutyl (meth)acrylate; N-(C₁-C₄, alkyl) amino (C₂-C₄ alkyl) (meth)acrylates, e.g., N-methyl-2-aminoethyl (meth)acrylate; and N,N-di(C₁-C₄ alkyl) amino (C₂-C₄ alkyl) (meth)acrylates, e.g., N,N-dimethyl-2-aminoethyl (meth)acrylate. The monomer may also comprise residues of salts of amine functional monomers, e.g., salts of those amine functional monomers as recited previously herein. Salts of the amine functional monomer residues may be formed by mixing a carboxylic acid, e.g., lactic acid, with the copolymer after completion of controlled radical polymerization.

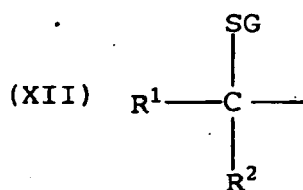
[0046] As described above, the copolymer may have nonionic moieties, ionic moieties and combinations thereof. In an embodiment of the present invention, the ethylenically unsaturated monomers can be selected from, for example, poly(alkylene glycol) (meth)acrylates; C₁-C₄ alkoxy poly(alkylene glycol) (meth)acrylates; hydroxyalkyl (meth)acrylates having from 2 to 4 carbon atoms in the alkyl group; N-(hydroxy C₁-C₄ alkyl) (meth)acrylamides, e.g., N-hydroxymethyl (meth)acrylamide and N-(2-hydroxyethyl) (meth)acrylamide; N,N-di-(hydroxy C₁-C₄ alkyl) (meth)acrylamides (e.g., N,N-di(2-hydroxyethyl) (meth)acrylamide); carboxylic acid functional monomers; salts of carboxylic acid functional monomers; amine functional monomers; salts of amine functional monomers; and mixtures thereof.

[0047] Poly(alkylene glycol) (meth)acrylates and C₁-C₄ alkoxy poly(alkylene glycol) (meth)acrylates are prepared by known methods. For example, (meth)acrylic acid or hydroxyalkyl (meth)acrylate, e.g., 2-hydroxyethyl (meth)acrylate, may be reacted with one or more alkylene oxides, e.g., ethylene oxide, propylene oxide and butylene oxide. Alternatively, an alkyl (meth)acrylate may be transesterified with a C₁-C₄ alkoxy poly(alkylene glycol), e.g., methoxy poly(ethylene glycol). Examples of poly(alkylene glycol) (meth)acrylates and C₁-C₄ alkoxy poly(alkylene glycol) (meth)acrylates include poly(ethylene glycol) (meth)acrylate and methoxy poly(ethylene glycol) (meth)acrylate, the poly(ethylene glycol) moiety of each having a molecular weight of from 100 to 800. An example of a commercially available C₁-C₄ alkoxy poly(alkylene glycol) (meth)acrylate is methoxy poly(ethylene glycol) 550 methacrylate monomer from Sartomer Company, Inc. Preferred hydroxy functional monomer are hydroxyalkyl (meth)acrylates having from 2 to 20 carbon atoms in the alkyl group; epoxide functional ethylenically unsaturated radically polymerizable monomers, which are hydrolyzed; hydroxyalkyl (meth)acrylates having from 2 to 20 carbon atoms in the alkyl group, which are reacted with a lactone; beta-hydroxy ester functional (meth)acrylates, which are the reaction product of (i) (meth)acrylic acid and a glycidyl ester of a saturated monocarboxylic acid having from 4 to 26 carbon atoms, or (ii) glycidyl (meth)acrylate and a saturated monocarboxylic acid having from 4 to 26 carbon atoms; and mixtures thereof.

[0048] The present invention is also directed to a non-random copolymer of general formula (XI):



where A and B are different compositions of ethylenically unsaturated monomers; p is an integer from 1 to 1,000; s is an integer from 1 to 1,000; t is an integer from 1, to 100; and ϕ is a residue from the iniferter initiator of the present invention. The residue ϕ typically has the structure of general formula XII:



where R¹ is selected from the group consisting of C₁-C₂₀ alkyl, cyclic, heterocyclic or alkynol; R² is selected from the group consisting of H and C₁-C₄ alkyl and SG is a radical stabilizing group as discussed above.

[0049] In an embodiment of the present invention, the copolymer can contain a segment that includes carboxylic acid functional monomers selected from (meth)acrylic acid, maleic anhydride, maleic acid, di(C₁-C₄ alkyl) maleates, itaconic acid, mono or di(C₁-C₄ alkyl) itaconates, and mixtures thereof. In a still further embodiment of the present invention, the copolymer segment is a residue of amine functional monomers selected from amino(C₂-C₄ alkyl) (meth)acrylates, N-(C₁-C₄ alkyl)amino(C₂-C₄ alkyl) (meth)acrylates, N,N-di(C₁-C₄ alkyl)amino(C₂-C₄ alkyl) (meth)acrylates and mixtures thereof.

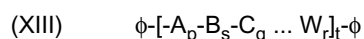
[0050] The copolymer also may contain a segment that contains cationic moieties selected from ammonium, sulpho-

nium and phosphonium. Ammonium, sulphonium and phosphonium moieties may be introduced into the (co)polymer by means known to the skilled artisan. For example, when the (co)polymer contains a residue of N,N-dimethyl-2-aminoethyl (meth)acrylate, the N,N-dimethylamino moieties may be converted to ammonium moieties by mixing an acid, e.g., lactic acid, with the polymer.

[0051] Further, the copolymer also may contain a segment that contains residues of oxirane functional monomers, such as glycidyl (meth)acrylate. The oxirane group may be left as is or it may be used to introduce sulphonium or phosphonium moieties into the polymer. Sulphonium moieties may be introduced into the polymer by reaction of the oxirane groups with thiodiethanol in the presence of an acid, such as lactic acid. Reaction of the oxirane groups with a phosphine, e.g., triphenyl phosphine or tributyl phosphine, in the presence of an acid, such as lactic acid, results in the introduction of phosphonium moieties into the graft (co)polymer.

[0052] Additionally, the copolymer may contain a segment that contains residues of hydroxy functional monomers, such as an hydroxyalkyl(meth)acrylate. Examples of hydroxyalkyl(meth)acrylates include hydroxyethyl(meth)acrylate and hydroxy(propyl)methacrylate.

[0053] The non-random copolymer of the present invention can have any number of monomers and monomer blocks as depicted by general structure XIII:



where A, B, C and W represent different compositions of ethylenically unsaturated monomers; p is an integer from 1 to 1,000; s, q and r are independently integers from 0 to 1,000; t is an integer from 1 to 100; and ϕ is a residue from the iniferter initiator as defined above.

[0054] Referring to general structure XI, when containing more than one type or species of monomer residue, the A- and B-blocks may each have at least one of block, e.g., di-block and tri-block, alternating and gradient architectures. Gradient architecture refers to a sequence of different monomer residues that changes gradually in a systematic and predictable manner along the polymer backbone. For purposes of illustration, an A-block containing 6 residues of methyl methacrylate (MMA) and 6 residues of glycidyl methacrylate (GMA), for which p is 12, may have di-block, tetra-block, alternating and gradient architectures as represented in general formulas XIV, XV, XVI, and XVII.

(XIV) Di-Block Architecture -(MMA-MMA-MMA-MMA-MMA-MMA-GMA-GMA-GMA-GMA-GMA-GMA)-

(XV) Tetra-Block Architecture -(MMA-MMA-MMA-GMA-GMA-GMA-MMA-MMA-MMA-GMA-GMA-GMA)-

(XVI) Alternating Architecture -(MMA-GMA-MMA-GMA-MMA-GMA-MMA-GMA-MMA-GMA-MMA-GMA)-

(XVII) Gradient Architecture -(MMA-MMA-MMA-GMA-MMA-MMA-GMA-GMA-MMA-GMA-GMA-GMA)-

The B-block may be described in a manner similar to that of the A-block.

[0055] The order in which monomer residues occur along the backbone of the block copolymer typically is determined by the order in which the corresponding monomers are fed into the vessel in which the controlled radical polymerization is conducted. For example, the monomers that are incorporated as residues in the A-block of the block copolymer are generally fed into the reaction vessel prior to those monomers that are incorporated as residues in the B-block.

[0056] During formation of the A- and B-blocks, if more than one monomer is fed into the reaction vessel at a time, the relative reactivities of the monomers typically determines the order in which they are incorporated into the living polymer chain. Gradient sequences of monomer residues within the A- and B-blocks can be prepared by the controlled radical polymerization of the present invention by (a) varying the ratio of monomers fed to the reaction medium during the course of the polymerization, (b) using a monomer feed containing monomers having different rates of polymerization, or (c) a combination of (a) and (b).

[0057] The copolymer of the present invention typically has a number average molecular weight (M_n) of from 500 to 1,000,000, preferably from 700 to 100,000 and most preferably from 800 to 10,000, as determined by gel permeation chromatography using polystyrene standards. The molecular weight distribution or polydispersity index (weight average molecular weight divided by the number average molecular weight, M_w/M_n) of the (co)polymer typically is less than 2.5, preferably less than 2.0, more preferably less than 1.8 and most preferably less than 1.5.

[0058] The copolymers of the present invention can be used without limitation, in film-forming compositions, as rheology modifiers, with pigment or ink dispersants, in gel matrices and with molding resins.

[0059] The copolymers of the present invention may be used in coatings. In a preferred embodiment, the coating is a thermosetting resin composition. The thermosetting coating composition of the present invention may be in the form of liquid coating compositions, examples of which include aqueous and solvent-based coating compositions and electrodepositable coating compositions. The present thermosetting coating composition may also be in the form of a co-reactable solid particulate composition, such as a powder coating composition. Regardless of the form, the present thermosetting coating composition may be pigmented or clear, and may be used alone or in combination as primers, basecoats or topcoats.

[0060] When used in thermosetting and coating compositions, the copolymers of the present invention, prepared using a monofunctional iniferter, have several advantages compared with (co)polymers prepared by other controlled polymerization techniques. For example, certain functional monomers, such as carboxylic acid functional monomers, may be polymerized directly, rather than having to use time consuming and expensive "blocking" and "deblocking" steps to prevent the carboxylic acid group from reacting with the initiator and effectively ending polymerization. The present method provides excellent controlled polymerization using such monomers directly, better, more predictable placement of the functional monomer and no post polymerization removal of the blocking agent.

[0061] Compared to atom and group transfer controlled radical polymerization techniques, the present monofunctional iniferter method provides several advantages. First, potentially corrosive halides are not used. This provides the ability to use a less expensive and broader range of materials of construction for manufacturing, storing, shipping and utilizing the copolymer of the present invention. Second, transition metals and special ligands, which must be removed after polymerization, are not used. Any residual from these materials can potentially cause degradation and discoloration of the eventual coating. Finally, the range of monomers that can be employed include any radically polymerizable compound, rather than the limited list that can be used with atom and group radical polymerization techniques.

[0062] Polymers prepared by ionic (anionic, cationic, etc.) polymerization techniques are even more restricted as to the monomers that can be used and the conditions that may be employed than the atom/group radical polymerization techniques.

[0063] Compared to the prior art, multifunctional iniferter methodologies, the present monofunctional iniferter provides advantages in coating compositions. First and foremost, the present copolymers do not contain the bulky, multifunctional initiator groups required in the prior art iniferter methods. When used in coating compositions, the smaller end groups of the present copolymers provide for lower viscosity, better flow properties, better leveling and better storage stability than similar copolymers prepared using the multifunctional iniferters of the prior art methods. Some of the practical benefits of these properties are lower VOC (volatile organic carbon) in liquid coatings as well as better flow and leveling in powder coatings and electrodeposition coatings. The iniferters of the present invention are also easier and less expensive to make, easier to use and can be prepared from commonly and commercially available starting materials.

[0064] The superior coating composition properties as well as the ease and less expense to prepare and use properties make the present monofunctional iniferter polymerization method and the resulting polymer compositions a significant advancement solving the problems and deficiencies of prior art controlled polymerization methods.

[0065] In an embodiment of the present invention, the coating composition is a co-reactable solid, particulate mixture of (a) a first reactant having functional groups and (b) a second reactant having functional groups, which may be the copolymer of the present invention. The second reactant (b) contains functional groups that can react with the functional groups of the first reactant. Referring to general structure I, when the second reactant is the present copolymer, it is characterized in that A and B are different compositions of ethylenically unsaturated monomers, with B including functional monomers with a functional group selected from the group consisting of oxirane, hydroxy and carboxylic acid.

[0066] Not wishing to be limited to any one set of functional groups, there are several examples of co-reactive functional groups that can be used in the present invention. The first or crosslinking reactant has a functional group different than that contained in the second reactant and is co-reactive toward the functional groups of the second reactant and can be, but is not limited to, epoxy or oxirane; carboxylic acid; hydroxy; polyol; isocyanate; capped isocyanate; amine; aminoplast and beta-hydroxyalkylamide. The functional groups of the second reactant can be, but are not limited to, epoxy, or oxirane; carboxylic acid; hydroxy; amide; oxazoline; aceto acetate; isocyanate; or carbamate.

[0067] Curable powder coating compositions typically comprise a polymer reactant having functional groups, for example, an epoxide functional polymer reactant, and a first reactant having functional groups that act as a crosslinking agent. The first reactant having functional groups has functional groups that are co-reactive towards and can form covalent bonds with the functional groups of the second reactant, a functionalized copolymer of the present invention. The first and second reactants of the curable powder coating composition may each independently comprise one or more functional species, and are each present in amounts sufficient to provide cured coatings having a desirable combination of physical properties, such as smoothness, clarity, solvent resistance and hardness.

[0068] Not wishing to be limited to any one set of functional groups, there are several examples of co-reactive functional groups that can be used in the present invention. One example of curable powder coating compositions from which the compositions of the present invention may be selected include powder coating compositions comprising an epoxide functional polymer as the first reactant and an epoxide reactive crosslinking agent, such as a carboxylic acid functional

crosslinking agent, as the second reactant. Examples of this type of powder coating are disclosed in United States Patent Nos. 5,407,707, 5,663,240 and 5,710,214. Another example is a powder coating composition comprising a carboxylic acid functional polymer as the first reactant and a beta-hydroxyalkylamide functional crosslinking agent as the second reactant, such as those disclosed in United States Patent Nos. 4,889,890, 4,937,288, 5,098,955, 5,202,382 and 5,214,101. A further example is a powder coating composition comprising an hydroxy functional polymer as the first reactant and capped isocyanate functional crosslinking agent as the second reactant, such as those described in United States Patent Nos. 4,997,900, 5,439,896, 5,508,337, 5,510,444, 5,554,692 and 5,777,061.

[0069] Polymers comprising the majority of the binder resins in curable powder coating compositions are solid at room temperature, typically having differential scanning calorimetry (DSC) derived glass transition midpoint values of from 30°C to 80°C, preferably from 35°C to 50°C. These polymers also typically have number average molecular weights (Mn) of from 500 to 15,000.

[0070] Classes of epoxide functional polymers from which the copolymer reactant of the curable powder coating compositions of the present invention may be selected include, but are not limited to, epoxide functional vinyl polymers, of which epoxide functional (meth)acrylic polymers, epoxide functional polyethers, epoxide functional polyesters and combinations thereof are included. Epoxide functional vinyl polymers can be prepared by the controlled free radical polymerization method of the present invention.

[0071] Epoxide functional vinyl polymers can be prepared using the controlled polymerization method of the present invention and are typically prepared by polymerizing one or more epoxide functional ethylenically unsaturated monomers with a non-epoxide functional ethylenically unsaturated monomer. Examples of non-epoxide functional ethylenically unsaturated monomers include, but are not limited to, methyl (meth)acrylate, isobornyl (meth)acrylate, butyl (meth)acrylate and styrene. Examples of epoxide functional ethylenically unsaturated monomers that may be used in the preparation of epoxide functional vinyl polymers include, but are not limited to, glycidyl (meth)acrylate, 3,4-epoxycyclohexylmethyl (meth)acrylate, 2-(3,4-epoxycyclohexyl)ethyl (meth)acrylate and allylglycidyl ether. Examples of ethylenically unsaturated monomers that are free of epoxide functionality include those described in U.S. Patent No. 5,407,707 at column 2, lines 17 through 56.

[0072] In a preferred embodiment of the present invention, the epoxide functional vinyl polymer, prepared using the method of the present invention, is prepared from a majority of (meth)acrylate monomers and is referred to herein as an "epoxide functional (meth)acrylic polymer." The epoxide functional vinyl polymer typically has a number average molecular weight of from 500 to 5,000, preferably from 800 to 2,500.

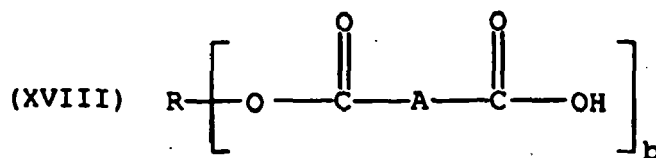
[0073] Epoxide functional polyethers can also be used in the present invention. Epoxide functional polyethers can be prepared from a hydroxyl functional monomer, such as a diol, and an epoxide functional monomer, and/or a monomer having both hydroxy and epoxide functionality. Suitable epoxide functional polyethers include, but are not limited to, those based on 4,4'-isopropylidenediphenol (bisphenol A), a specific example of which is EPON® RESIN 2002 available commercially from Shell Chemicals.

[0074] Epoxide functional polyesters can be used as the first reactant having functional groups and can be prepared by art-recognized methods, which typically include first preparing a hydroxyl functional polyester that is then reacted with epichlorohydrin. Polyesters having hydroxyl functionality may be prepared by art-recognized methods, which include reacting carboxylic acids (and/or esters thereof) having acid(or ester) functionalities of at least 2, and polyols having hydroxyl functionalities of at least 2. As is known to those of ordinary skill in the art, the molar equivalents ratio of carboxylic acid groups to hydroxyl groups of the reactants is selected such that the resulting polyester has hydroxy functionality and the desired molecular weight.

[0075] Examples of multifunctional carboxylic acids useful in preparing hydroxyl functional polyesters are known to the skilled artisan and include, for example, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, isophthalic acid and terephthalic acid. Examples of polyols useful in preparing hydroxy functional polyesters are known to those skilled in the art and include, for example, glycerin, trimethylolpropane, ethylene glycol and 1,4-dimethylolcyclohexane.

[0076] Epoxide reactive crosslinking agents that are used in thermosetting powder coating compositions comprising epoxide functional polymers may have functional groups selected from hydroxyl, thiol, primary amines, secondary amines, carboxyl and mixtures thereof. Useful epoxide reactive crosslinking agents having amine functionality include, for example, dicyandiamide and substituted dicyandiamides. Preferably, the epoxide reactive crosslinking agent has carboxylic acid groups. In one embodiment of the present invention, the epoxide reactive crosslinking agent has carboxylic acid functionality and is substantially crystalline. By "crystalline" is meant that the co-reactant contains at least some crystalline domains, and correspondingly may contain some amorphous domains. While not necessary, it is preferred that the epoxide reactive crosslinking agent have a melt viscosity less than that of the epoxy functional polymer (at the same temperature). As used herein, by "epoxide reactive crosslinking agent" is meant that the epoxide reactive crosslinking agent has at least two functional groups that are reactive with epoxide functionality.

[0077] Other suitable carboxylic acid functional crosslinking agents include those represented by the following general formula XVIII:



wherein R is a residue from a polyol, A is a divalent linking group having from 1 to 10 carbon atoms, and b is an integer of from 2 to 10. Examples of polyols from which R of general formula XVIII may be derived include, but are not limited to, ethylene glycol, di(ethylene glycol), trimethylolethane, trimethylolpropane, pentaerythritol, di-trimethylolpropane, di-pentaerythritol and mixtures thereof. Divalent linking groups from which A may be selected include, but are not limited to, methylene; ethylene; propylene; isopropylene; butylene; pentylene; hexylene; heptylene; octylene; nonylene; decylene; cyclohexylene, such as 1,2-cyclohexylene; substituted cyclohexylene, such as 4-methyl-1,2-cyclohexylene; phenylene, such as 1,2-phenylene; and 4-carboxylic acid-1,2-phenylene. The divalent linking group A is preferably aliphatic.

[0078] The crosslinking agent represented by general formula XVIII is typically prepared from a polyol and a dibasic or cyclic anhydride. For example, trimethylol propane and hexahydro-4-methylphthalic anhydride are reacted together in a molar ratio of 1:3, respectively, to form a carboxylic acid functional crosslinking agent. This particular crosslinking agent can be described with reference to general formula XVIII as follows, R is the residue of trimethylol propane, A is the divalent linking group 4-methyl-1,2-cyclohexylene, and b is 3. Carboxylic acid functional crosslinking agents described herein with reference to general formula XVIII are meant to include also any unreacted starting materials and/or coproducts, for example oligomeric species, resulting from their preparation and contained therein.

[0079] Curable powder coating compositions comprising epoxide functional (co)polymer and epoxide reactive crosslinking agent usually also include one or more cure catalysts for catalyzing the reaction between the reactive functional groups and the epoxide groups of the polymer. Examples of cure catalysts for use with acid functional crosslinking agents include tertiary amines, such as methyl dicocoamine, and tin compounds such as triphenyl tin hydroxide. The curing catalyst is typically present in the curable powder coating composition in an amount of less than 5 percent by weight, preferably from 0.25 to 2.0 percent by weight, based on the total resin solids weight of the composition.

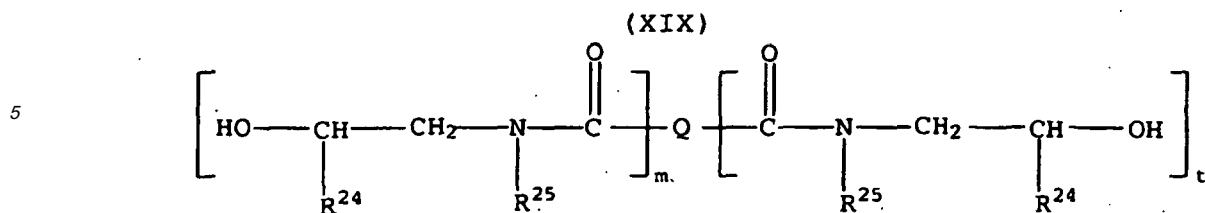
[0080] Curable powder coating compositions that include epoxide functional copolymers and epoxide reactive crosslinking agents typically have present therein epoxide functional copolymers in an amount of from 60 to 95 percent by weight based on the total resin solids weight of the composition, preferably from 70 to 85 percent by weight, based on the total resin solids weight composition. The epoxide reactive crosslinking agent is typically present in the curable powder coating composition in an amount corresponding to the balance of these recited ranges, 5 to 40, preferably 15 to 30 percent by weight. The equivalent ratio of epoxide equivalents in the epoxide functional copolymer to the equivalents of reactive functional groups is typically from 0.5:1 to 2:1, preferably from 0.8:1 to 1.5:1. Curable powder coating compositions comprising carboxylic acid functional crosslinking agent are typically cured at a temperature of from 121°C to 177°C over a period of from 10 to 60 minutes.

[0081] Curable powder coating compositions comprising carboxylic acid functional copolymer as the second reactant (b) and beta-hydroxyalkylamide functional crosslinking agent as the first reactant (a) are also useful in the present invention. Classes of useful carboxylic acid functional copolymers include, but are not limited to, carboxylic acid functional vinyl polymers, carboxylic acid functional polyesters, carboxylic acid functional polyurethanes, and mixtures thereof.

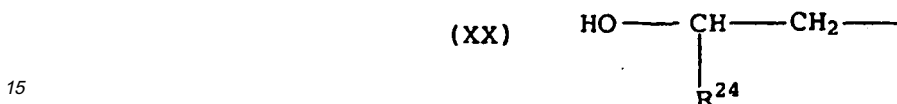
[0082] As discussed above, carboxylic acid functional vinyl copolymers can be prepared by the controlled radical polymerization method of the present invention. The carboxylic acid functional vinyl copolymer is typically prepared by polymerizing one or more carboxylic acid functional ethylenically unsaturated monomers, such as (meth)acrylic acid, with one or more ethylenically unsaturated monomers that are free of carboxylic acid functionality, such as, ethyl (meth)acrylate, isobornyl (meth)acrylate, butyl (meth)acrylate and styrene. Alternatively, the carboxylic acid functional vinyl (co)polymer that is then reacted with a cyclic anhydride, such as succinic anhydride.

[0083] Carboxylic acid functional polyurethanes may be prepared by reacting polyols and polyisocyanates so as to form a polyurethane polyol, which is then reacted with polycarboxylic acid or cyclic anhydride to introduce free carboxylic acid into the reaction product. Carboxylic functional polyurethane that may be used in the curable powder coating compositions, which include beta-hydroxyalkylamide crosslinking agents are described in further detail in U.S. Patent No. 4,937,288 at column 6, lines 13 through 39.

[0084] One or more beta-hydroxyalkylamide crosslinking agents may be present in the curable powder coating compositions comprising carboxylic acid functional copolymer as the second reactant. The beta-hydroxyalkylamide crosslinking agent can be represented by the following general formula XIX:



where R^{24} is H or $\text{C}_1\text{-C}_5$ alkyl; R^{25} is H or $\text{C}_1\text{-C}_5$ alkyl or a structure as defined by structure XX:



for which R^{24} is as described above, Q is a chemical bond or monovalent or polyvalent organic radical derived from saturated, unsaturated or aromatic hydrocarbon radicals including substituted hydrocarbon radicals containing from 2 to 20 carbon atoms, m equals 1 or 2, t equals 0 to 2, and $m + t$ is at least 2. Preferably, Q is an alkylene radical $-(\text{CH}_2)_x$ -where x is equal to 2 to 12, preferably 4 to 10; m is equal to 1 to 2, t is equal to 0 to 2, and $m + t$ is at least 2, preferably greater than 2 up to and including 4. The beta-hydroxyalkylamide crosslinking agent represented by general formula XVIII can be prepared by art recognized methods, as described in, for example, U.S. Patent No. 4,937,288 at column 7, lines 6 through 16.

[0085] Curable powder coating compositions comprising carboxylic acid functional copolymer and beta-hydroxyalkylamide crosslinking agent typically have present therein carboxylic acid functional copolymer in an amount of from 60 to 95 percent by weight, based on total resin solids weight of the composition, preferably from 80 to 90 percent by weight, based on total resin solids weight of the composition. The beta-hydroxyalkylamide crosslinking agent is typically present in the curable powder coating composition in an amount corresponding to the balance of the recited ranges, 5 to 40, preferably 10 to 20 percent by weight.

[0086] To achieve a suitable level of cure, the equivalent ratio of hydroxy equivalents in the beta-hydroxyalkylamide crosslinking agent to carboxylic acid equivalents in the carboxylic acid functional copolymer is preferably from 0.6:1 to 1.6:1, preferably from 0.8:1 to 1.3:1. Ratios outside the range of 0.6:1 to 1.6:1 are generally undesirable due to the resulting poor cure response associated therewith.

[0087] Curable powder coating compositions comprising carboxylic acid functional copolymer and beta-hydroxyalkylamide functional crosslinking agent are typically cured at a temperature of from 149°C to 204°C over a period of from 10 to 60 minutes.

[0088] Also useful in the present invention are curable powder coating compositions comprising hydroxy functional copolymer, made using the method of the present invention, and capped isocyanate functional crosslinking agent. Hydroxy functional copolymers that can be used in such compositions include, but are not limited to, hydroxy functional vinyl copolymers, hydroxy functional polyesters, hydroxy functional polyurethanes and mixtures thereof.

[0089] Vinyl copolymers having hydroxy functionality can be prepared by the controlled radical polymerization method of the present invention. In an embodiment of the present invention, the hydroxy functional vinyl copolymer is prepared from a majority of (meth)acrylic monomers and is referred to herein as a "hydroxy functional (meth)acrylic copolymer."

[0090] Hydroxy functional polyesters useful in curable powder coating compositions comprising capped isocyanate functional crosslinking agent can be prepared by art-recognized methods. Typically, diols and dicarboxylic acids or diesters of dicarboxylic acids are reacted in a proportion such that the molar equivalents of hydroxy groups is greater than that of carboxylic acid groups (or esters of carboxylic acid groups) with the concurrent removal of water or alcohols from the reaction medium. Hydroxy functional polyesters useful in the present invention are described in further detail in U.S. Patent No. 5,508,337 at column 5, line 24 through column 6, line 30.

[0091] Hydroxy functional urethanes can be prepared by art-recognized methods, for example, as previously described herein. Hydroxy functional urethanes useful in the present invention are described in further detail in U.S. Patent 5,510,444 at column 5, line 33 through column 7, line 61.

[0092] By "capped isocyanate crosslinking agent" is meant a crosslinking agent having two or more capped isocyanate groups that can decap (or deblock) under cure conditions, for example, at elevated temperature, to form free isocyanate groups and free capping groups. The free isocyanate groups formed by decapping of the crosslinking agent are preferably capable of reacting and forming substantially permanent covalent bonds with the hydroxy groups of hydroxy functional

polymer.

[0093] It is desirable that the capping group of the capped isocyanate crosslinking agent not adversely affect the curable powder coating composition upon decapping from the isocyanate, for example, when it becomes a free capping group. For example, it is desirable that the free capping group neither become trapped in the cured film as gas bubbles nor excessively plasticize the cured film. Capping groups useful in the present invention preferably have the characteristics of being nonfugitive or capable of escaping substantially from the forming coating prior to its vitrification.

[0094] Classes of capping groups of the capped isocyanate crosslinking agent may be selected from: hydroxy functional compounds, such as ethylene glycol butyl ether, phenol and p-hydroxy methylbenzoate; 1H-azoles, such as 1H-1,2,4-triazole and 1H-2,5-dimethyl pyrazole; lactams, such as ε-caprolactam and 2-pyrrolidone; ketoximes, such as 2-propane oxime and 2-butanone oxime and those described in U.S. Patent No. 5,508,337 at column 7, lines 11 through 22, the disclosure of which is incorporated herein by reference. Other capping groups include morpholine, 3-aminopropyl morpholine and n-hydroxy phthalimide.

[0095] The isocyanate or mixture of isocyanates of the capped isocyanate crosslinking agent has two or more isocyanate groups and is preferably solid at room temperature. Examples of suitable isocyanates that may be used to prepare the capped isocyanate crosslinking agent include monomeric diisocyanates, such as α, α'-xylene diisocyanate, α, α', α'-tetramethylxylylene diisocyanate and 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (isophorone diisocyanate or IPDI), and dimers and trimers of monomeric diisocyanates containing isocyanurate, uretidino, biuret or allophanate linkages, such as the trimer of IPDI. Isocyanates that are useful in the present invention are described in further detail in U.S. Patent No. 5,777,061 at column 3; line 4 through column 4, line 40, the disclosure of which is incorporated herein by reference. A particularly preferred isocyanate is a trimer of 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane.

[0096] The capped isocyanate crosslinking agent may also be selected from oligomeric capped isocyanate functional adducts. As used herein, by "oligomeric capped polyisocyanate functional adduct" is meant a material that is substantially free of polymeric chain extension. Oligomeric capped polyisocyanate functional adducts can be prepared by art-recognized methods from, for example, a compound containing three or more active hydrogen groups, such as trimethylolpropane (TMP); and an isocyanate monomer, such as 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (IPDI) in a molar ratio of 1:3 respectively. In the case of TMP and IPDI, by employing art-recognized starved feed and/or dilute solution synthesis techniques, an oligomeric adduct having an average isocyanate functionality of 3 can be prepared ("TMP-3IPDI"). The three free isocyanate groups per TMP-3IPDI adduct are then capped with a capping group, such as 2-propane oxime or ε-caprolactam.

[0097] Another isocyanate useful in the present invention is TMDI, which is a mixture of 2,9,4-trimethyl hexamethylene diisocyanate and 2,2,4-trimethyl hexamethylene diisocyanate.

[0098] To catalyze the reaction between the isocyanate groups of the capped polyisocyanate crosslinking agent and the hydroxy groups of the hydroxy functional polymer, one or more catalysts are typically present in the powder coating composition in amounts of from, for example, 0.1 to 5 percent by weight, based on total resin solids of the composition. Classes of useful catalysts include metal compounds, in particular, organic tin compounds, such as tin(II) octanoate and dibutyltin(IV) dilaurate, and tertiary amines, such as diazabicyclo[2.2.2]octane. Examples of organic tin compounds and tertiary amines are described in U.S. Patent No. 5,508,337 at column 7, lines 28 through 49, the disclosure of which is incorporated herein by reference.

[0099] Curable powder coating compositions of the present invention include those where the second reactant is selected from acid functional copolymers and the first reactant is a glycidyl isocyanurates and/or a bisphenol A epoxide.

[0100] Curable powder coating compositions comprising hydroxy functional polymer and capped isocyanate functional crosslinking agent typically have present therein hydroxy functional copolymer in an amount of from 55 to 95 percent by weight, based on total resin solids weight of the composition, preferably from 75 to 90 percent by weight based on total resin solids weight of the composition. The capped isocyanate functional crosslinking agent is typically present in the powder composition in an amount corresponding to the balance of these recited ranges, 5 to 45, preferably 10 to 25 percent by weight.

[0101] The equivalent ratio of isocyanate equivalents in the capped isocyanate crosslinking agent to hydroxy equivalents in the capped isocyanate crosslinking agent to hydroxy equivalents in the hydroxy functional copolymer is typically within the range of 1:3 to 3:1, preferably 1:2 to 2:1. While equivalent ratios outside of this range can be employed, that they are generally less desirable due to performance deficiencies in cured films obtained therefrom. Powder coating compositions comprising hydroxy functional polymer and capped isocyanate functional crosslinking agent are typically cured at a temperature of from 120°C to 190°C over a period of from 10 to 60 minutes.

[0102] Curable powder coating compositions may optionally contain additives such as waxes to improve the slip properties of the cured coating, degassing additives such as benzoin, adjuvant resin to modify and optimize coating properties, antioxidants and ultraviolet (UV) light absorbers. Examples of useful antioxidants and UV light absorbers include those available commercially from Ciba Specialty Chemicals under the trade names IRGANOX and TINUVIN. These optional additives, when used, are typically present in amounts up to 20 percent by weight, based on total weight

of resin solids of the curable composition.

[0103] Curable powder coating compositions useful in the present invention are typically prepared by first dry blending the functional copolymer, for example epoxide functional copolymer; the crosslinking agent; the polymeric flow control agent and additives such as degassing agent and catalysts in a blender, such as a Henshel blade blender. The blender is operated for a period of time sufficient to result in a homogeneous dry blend of the materials charged thereto. The homogeneous dry blend is then melt blended in an extruder, such as a twin screw co-rotating extruder, operated within a temperature range sufficient to melt but not gel the components. For example, when preparing curable powder coating compositions comprising epoxide functional crosslinking agent, the extruder is typically operated within a temperature range of from 80°C to 140°C, preferably from 100°C to 125°C.

[0104] Optionally, curable powder coating compositions of the present invention may be melt blended in two or more steps. For example, a first melt blend is prepared in the absence of cure catalyst. A second melt blend is prepared at a lower temperature, from a dry blend of the first melt blend and the cure catalyst. The melt blend curable powder coating composition is typically milled to an average particle size of from, for example, 15 to 30 microns.

[0105] In another embodiment of the present invention, the copolymer may be used in a thermosetting composition as a flow control agent, a resinous binder or as an additive in combination with a separate resinous binder, which may be prepared using the method of the present invention. Referring to general structure I, the present copolymer can be characterized in that A and B are different compositions of ethylenically unsaturated monomers, with B including functional monomers with a functional group selected, for example, from oxirane, hydroxy or carboxylic acid. When used as an additive, the non-random polymer as described herein may have low functionality (it may be monofunctional) and a correspondingly high equivalent weight. Alternatively, for other applications such as use as a reactive diluent, the additive may be highly functional with a correspondingly low equivalent weight.

[0106] The thermosetting composition of the present invention further comprises a crosslinking agent having at least two functional groups that are reactive with the functional groups of the copolymer reactant.

[0107] Not wishing to be limited to any one set of functional groups, there are several examples of co-reactive functional groups that can be used in the present invention. The crosslinking reactant has a functional group different than that contained in the copolymer reactant and is co-reactive toward the functional groups of the copolymer reactant and can be, but is not limited to, epoxy or oxirane; carboxylic acid; hydroxy; polyol; isocyanate; capped isocyanate; amine; aminoplast and beta-hydroxyalkylamide. The functional groups of the copolymer reactant can be, but are not limited to, epoxy, or oxirane; carboxylic acid; hydroxy; amide; oxazoline; aceto acetate; isocyanate; or carbamate.

[0108] The copolymer is typically present in the thermosetting composition of the present invention in an amount of at least 0.5 percent by weight (when used as an additive), preferably at least 10 percent by weight (when used as a resinous binder), and more preferably at least 25 percent by weight, based on the total weight of resin solids of the thermosetting composition. The thermosetting composition also typically contains functionality polymer present in an amount of less than 99.5 percent by weight, preferably less than 90 percent by weight, and more preferably less than 75 percent by weight, based on the total weight of resin solids of the thermosetting composition. The copolymer may be present in the thermosetting composition of the present invention in an amount ranging between any combination of these values, inclusive of the recited values.

[0109] When the copolymer has hydroxyl functionality, examples of suitable crosslinking agents include aminoplasts containing methylol and/or methylol ether groups and polyisocyanates.

[0110] Aminoplasts are obtained from the reaction of formaldehyde with an amine or amide. The most common amines or amides are melamine, urea, or benzoguanamine, and are preferred. However, condensates with other amines or amides can be used; for example, aldehyde condensates of glycoluril, which give a high melting crystalline product which is useful in powder coatings. While the aldehyde used is most often formaldehyde, other aldehydes such as acetaldehyde, crotonaldehyde, and benzaldehyde may be used.

[0111] The aminoplast contains methylol groups and preferably at least a portion of these groups are etherified with an alcohol to modify the cure response. Any monohydric alcohol may be employed for this purpose including methanol, ethanol, butanol, isobutanol, and hexanol.

[0112] Preferably, the aminoplasts which are used are melamine-, urea-, or benzoguanamine-formaldehyde condensates etherified with an alcohol containing from one to four carbon atoms.

[0113] Other suitable crosslinking agents for hydroxy functional copolymers include polyisocyanates. The polyisocyanate crosslinking agent may be a fully capped polyisocyanate with substantially no free isocyanate groups, or it may contain free isocyanate functionality. Free isocyanate groups allow for curing of the composition at temperatures as low as ambient. When the crosslinking agent contains free isocyanate groups, the film-forming composition is preferably a two-package composition (one package comprising the crosslinking agent and the other comprising the hydroxyl functional polymer) in order to maintain storage stability.

[0114] The polyisocyanate can be an aliphatic or an aromatic polyisocyanate or a mixture of the two. Diisocyanates are preferred, although higher polyisocyanates can be used in place of or in combination with diisocyanates.

[0115] Examples of suitable aliphatic diisocyanates are straight chain aliphatic diisocyanates such as 1,4-tetrameth-

ylene diisocyanate and 1,6-hexamethylene diisocyanate. Also, cycloaliphatic diisocyanates can be employed. Examples include isophorone diisocyanate and 4,4'-methylene-bis-(cyclohexyl isocyanate). Examples of suitable aromatic diisocyanates are p-phenylene diisocyanate, diphenylmethane-4,4'-diisocyanate and 2,4- or 2,6-toluene diisocyanate. Examples of suitable higher polyisocyanates are triphenylmethane-4,4',4"-triisocyanate, 1,2,4-benzene triisocyanate and polymethylene polyphenyl isocyanate. Biurets and isocyanurates of diisocyanates, including mixtures thereof, such as the isocyanurate of hexamethylene diisocyanate, the biuret of hexamethylene diisocyanate and the isocyanurate of isophorone diisocyanate are also suitable.

[0116] Isocyanate prepolymers, for example, reaction products of polyisocyanates with polyols such as neopentyl glycol and trimethylol propane or with polymeric polyols such as polycaprolactone diols and triols (NCO/OH equivalent ratio greater than one) can also be used.

[0117] Any suitable aliphatic, cycloaliphatic, or aromatic alkyl monoalcohol or phenolic compound may be used as a capping agent for the capped polyisocyanate crosslinking agent in the composition of the present invention including, for example, lower aliphatic alcohols such as methanol, ethanol, and n-butanol; cycloaliphatic alcohols such as cyclohexanol; aromatic-alkyl alcohols such as phenyl carbinol and methylphenyl carbinol; and phenolic compounds such as phenol itself and substituted phenols wherein the substituents do not affect coating operations, such as cresol and nitrophenol. Glycol ethers may also be used as capping agents. Suitable glycol ethers include ethylene glycol butyl ether, diethylene glycol butyl ether, ethylene glycol methyl ether and propylene glycol methyl ether.

[0118] Other suitable capping agents include oximes such as methyl ethyl ketoxime, acetone oxime and cyclohexanone oxime, lactams such as epsilon-caprolactam, and amines such as dibutyl amine.

[0119] When the functionality of monomer composition B is an oxirane or epoxy group, the crosslinking agent has at least two functional groups that are reactive with epoxides. The at least two functional groups are intended to include mixtures of functional groups. The functional groups that are reactive with epoxides include, but are not limited to, polyamines, polyamides, polycarboxylic acids, polyanhydrides and polyphenolic compounds.

[0120] Suitable polyamines include, but are not limited to, amine and amide functional addition polymers and oligomers typically used in film-forming compositions such as acrylic and vinyl polymers.

[0121] Suitable polycarboxylic acids include, but are not limited to, dodecanedioic acid, azelaic acid, adipic acid, 1,6-hexanedioic acid, succinic acid, sebacic acid, maleic acid, citric acid, itaconic acid, pimelic acid, aconitic acid, carboxylic acid terminated polyesters, half-esters formed from reacting an anhydride with a polyol, carboxylic acid containing polymers such as acrylic acid and methacrylic acid containing polymers, polyesters and polyurethanes, fatty diacids and mixtures thereof.

[0122] Suitable polyanhydrides include addition polymers and oligomers typically used in film-forming compositions such as acrylic and vinyl polymers. Examples include, but are not limited to, those described in U.S. Patent Nos. 4,798,746 and 4,732,790.

[0123] When the copolymer has carboxylic acid functionality, the crosslinking agent is a beta-hydroxyalkylamide as described above.

[0124] The crosslinking agent is typically present in the thermosetting compositions of the present invention in an amount of at least 10 percent by weight, preferably at least 25 percent by weight, based on total resin solids weight of the composition. The crosslinking agent is also typically present in the composition in an amount of less than 90 percent by weight, preferably less than 75 percent by weight, based on total resin solids weight of the composition. The amount of crosslinking agent present in the thermosetting composition of the present invention may range between any combination of these values, inclusive of the recited values.

[0125] The equivalent ratio of functional groups in the polymer to reactive functional groups in the crosslinking agent is typically within the range of 1:0.5 to 1:1.5, preferably 1:0.8 to 1:1.2.

[0126] Usually the thermosetting composition will also preferably contain catalysts to accelerate the cure of the crosslinking agent with reactive groups on the polymer(s).

[0127] Suitable catalysts for aminoplast cure include acids such as acid phosphates and sulfonic acid or a substituted sulfonic acid. Examples include dodecylbenzene sulfonic acid, paratoluene sulfonic acid, phenyl acid phosphate, ethylhexyl acid phosphate, and the like. Suitable catalysts for isocyanate cure include organotin compounds such as dibutyltin oxide, dioctyltin oxide, dibutyltin dilaurate, and the like. The catalyst is usually present in an amount of about 0.05 to about 5.0 percent by weight, preferably about 0.25 to about 2.0 percent by weight, based on the total weight of resin solids in the thermosetting composition.

[0128] The thermosetting composition of the present invention is preferably used as a film-forming (coating) composition, and may contain adjunct ingredients conventionally used in such compositions. Optional ingredients such as, for example, plasticizers, surfactants, thixotropic agents, anti-gassing agents, organic cosolvents, flow controllers, anti-oxidants, UV light absorbers and similar additives conventional in the art may be included in the composition. These ingredients are typically present at up to about 40% by weight based on the total weight of resin solids.

[0129] The thermosetting composition of the present invention is typically a liquid and may be waterborne, but is usually solventborne. Suitable solvent carriers include the various esters, ethers, and aromatic solvents, including mix-

tures thereof, that are known in the art of coating formulation. The composition typically has a total solids content of about 40 to about 80 percent by weight.

[0130] The thermosetting composition of the present invention may contain color pigments conventionally used in surface coatings and may be used as a monocoat; that is, a pigmented coating. Suitable color pigments include, for example, inorganic pigments such as titanium dioxide, iron oxides, chromium oxide, lead chromate, and carbon black, and organic pigments such as phthalocyanine blue and phthalocyanine green. Mixtures of the above mentioned pigments may also be used. Suitable metallic pigments include in particular aluminum flake, copper bronze flake and metal oxide coated mica, nickel flakes, tin flakes, and mixtures thereof.

[0131] In general, the pigment is incorporated into the coating composition in amounts up to about 80 percent by weight based on the total weight of coating solids. The metallic pigment is employed in amounts of about 0.5 to about 25 percent by weight based on the total weight of coating solids.

[0132] As stated above, the thermosetting compositions of the present invention may be used in a method of coating a substrate comprising applying a thermosetting composition to the substrate, coalescing the thermosetting composition over the substrate in the form of a substantially continuous film, and curing the thermosetting composition.

[0133] The compositions can be applied to various substrates to which they adhere including wood, metals, glass, and plastic. The compositions can be applied by conventional means including brushing, dipping, flow coating, spraying and the like, but they are most often applied by spraying. The usual spray techniques and equipment for air spraying and electrostatic spraying and either manual or automatic methods can be used.

[0134] After application of the composition to the substrate, the composition is allowed to coalesce to form a substantially continuous film on the substrate. Typically, the film thickness will be about 0.01 to about 5 mils (about 0.254 to about 127 microns), preferably about 0.1 to about 2 mils (about 2.54 to about 50.8 microns) in thickness. The film is formed on the surface of the substrate by driving solvent, i.e., organic solvent and/or water, out of the film by heating or by an air drying period. Preferably, the heating will only be for a short period of time, sufficient to ensure that any subsequently applied coatings can be applied to the film without dissolving the composition. Suitable drying conditions will depend on the particular composition, but in general a drying time of from about 1 to 5 minutes at a temperature of about 68-250°F (20-121°C) will be adequate. More than one coat of the composition may be applied to develop the optimum appearance. Between coats the previously applied coat may be flashed, that is, exposed to ambient conditions for about 1 to 20 minutes.

[0135] The film-forming composition of the present invention is preferably used as the clear coat layer in a multi-component composite coating composition such as a "color-plus-clear" coating system, which includes at least one pigmented or colored base coat and at least one clear topcoat. In this embodiment, the clear film-forming composition may include the thermosetting composition of the present invention.

[0136] The film-forming composition of the base coat in the color-plus-clear system can be any of the compositions useful in coatings applications, particularly automotive applications. The film-forming composition of the base coat comprises a resinous binder and a pigment to act as the colorant. Particularly useful resinous binders are acrylic polymers, polyesters, including alkyds, and polyurethanes. Polymers prepared using atom transfer radical polymerization may also be used as resinous binders in the base coat.

[0137] The base coat compositions may be solventborne or waterborne. Waterborne base coats in color-plus-clear compositions are disclosed in U. S. Patent No. 4,403,003, and the resinous compositions used in preparing these base coats can be used in the practice of this invention. Also, waterborne polyurethanes such as those prepared in accordance with U. S. Patent No. 4,147,679 can be used as the resinous binder in the base coat. Further, waterborne coatings such as those described in U. S. Patent No. 5,071,904 can be used as the base coat.

[0138] The base coat contains pigments to give it color. Suitable pigments include those discussed above. In general, the pigment is incorporated into the coating composition in amounts of about 1 to 80 percent by weight based on weight of coating solids. Metallic pigment is employed in amounts of about 0.5 to 25 percent by weight based on weight of coating solids.

[0139] If desired, the base coat composition may contain additional materials well-known in the art of formulated surface coatings, including those discussed above. These materials can constitute up to 40 percent by weight of the total weight of the coating composition.

[0140] The base coating compositions can be applied to various substrates to which they adhere by conventional means, but they are most often applied by spraying. The usual spray techniques and equipment for air spraying and electrostatic spraying and either manual or automatic methods can be used.

[0141] During application of the base coat composition to the substrate, a film of the base coat is formed on the substrate. Typically, the base coat thickness will be about 0.01 to 5 mils (0.254 to 127 microns), preferably 0.1 to 2 mils (2.54 to 50.8 microns) in thickness.

[0142] After application of the base coat to the substrate, a film is formed on the surface of the substrate by driving solvent out of the base coat film by heating or by an air drying period, sufficient to ensure that the clear coat can be applied to the base coat without the former dissolving the base coat composition, yet insufficient to fully cure the base coat. More than one base coat and multiple clear coats may be applied to develop the optimum appearance. Usually

between coats, the previously applied coat is flashed.

[0143] The clear topcoat composition may be applied to the base coated substrate by any conventional coating technique such as brushing, spraying, dipping or flowing, but spray applications are preferred because of superior gloss. Any of the known spraying techniques may be employed such as compressed air spraying, electrostatic spraying and either manual or automatic methods.

[0144] After application of the clear coat composition to the base coat, the coated substrate may be heated to cure the coating layer(s). In the curing operation, solvents are driven off and the film-forming materials in the composition are crosslinked. The heating or curing operation is usually carried out at a temperature in the range of from at least ambient (in the case of free polyisocyanate crosslinking agents) to 350°F (ambient to 177°C) but if needed, lower or higher temperatures may be used as necessary to activate crosslinking mechanisms.

[0145] In a further embodiment of the present invention, the present copolymer is included in thermosetting compositions used in the electrocoating of conductive substrates. Referring to structure I, the monomer composition A includes monomers that contain active hydrogens and monomers that contain onium salt groups. The coating composition further contains curing agents, which are reactive with the active hydrogen groups of the polymer. The active hydrogen-containing polymers are prepared by the method of this invention, and have well defined polymer chain structures, molecular weights and molecular weight distributions.

[0146] The active hydrogen group-containing polymer containing onium salt groups may be present in the thermosetting compositions of the invention as a resinous binder (i.e., a film-forming polymer) or as an additive in combination with a separate resinous binder, which may be prepared either by atom transfer radical polymerization or by conventional polymerization methods. When used as an additive, for example as a reactive diluent, the active hydrogen group-containing polymer as described herein typically has a high degree of functionality and a correspondingly low equivalent weight. However, it should be appreciated that for other applications, the additive may have low functionality (it may be monofunctional) and a correspondingly high equivalent weight. The active hydrogen group-containing polymer containing onium salt groups is typically present in the thermosetting compositions of the invention in an amount of at least 0.5 percent by weight (when used as an additive) and in an amount of at least 25 percent by weight (when used as a resinous binder), based on total weight of resin solids of the thermosetting composition. The active hydrogen group-containing polymers are also typically present in the thermosetting compositions in an amount of less than 95 percent by weight, and preferably in an amount of less than 80 percent by weight, based on total weight of resin solids of the thermosetting composition. The active hydrogen group-containing polymer may be present in the thermosetting compositions of the invention in an amount ranging between any combination of these values, inclusive of the recited values.

[0147] The thermosetting composition of the present invention further comprises (b) a curing agent having at least two functional groups which are reactive with the active hydrogen groups of the polymer (a) described above.

[0148] Examples of suitable curing agents for use in the thermosetting compositions of the invention include polyisocyanate and aminoplast curing agents. The preferred curing agents for use in thermosetting compositions of the invention, particularly for cationic electrodeposition, are blocked organic polyisocyanates. The polyisocyanates can be fully blocked as described in U. S. Patent No. 3,984,299 column 1, lines 1 to 68, column 2, and column 3, lines 1 to 15, or partially blocked and reacted with the polymer backbone as described in U. S. Patent No. 3,947,338 column 2, lines 65 to 68, column 3, and column 4, lines 1 to 30, which are incorporated by reference herein. By "blocked" is meant that the isocyanate groups have been reacted with a compound so that the resultant blocked isocyanate group is stable to active hydrogens at ambient temperature but reactive with active hydrogens in the film forming polymer at elevated temperatures usually between 90°C and 200°C.

[0149] Suitable polyisocyanates include aromatic and aliphatic polyisocyanates, including cycloaliphatic polyisocyanates and representative examples include diphenylmethane-4,4'-diisocyanate (MDI), 2,4- or 2,6-toluene diisocyanate (TDI), including mixtures thereof, p-phenylene diisocyanate, tetramethylene and hexamethylene diisocyanates, dicyclohexylmethane-4,4'-diisocyanate, isophorone diisocyanate, mixtures of phenylmethane-4,4'-diisocyanate and polymethylene polyphenylisocyanate. Higher polyisocyanates such as triisocyanates can be used. An example would include triphenylmethane-4,4',4"-triisocyanate. Isocyanate prepolymers with polyols such as neopentyl glycol and trimethylolpropane and with polymeric polyols such as polycaprolactone diols and triols (NCO/OH equivalent ratio greater than 1) can also be used.

[0150] The polyisocyanate curing agent is typically utilized in conjunction with the active hydrogen group-containing polymer (a) in an amount of at least 1 percent by weight, preferably at least 15 percent by weight, and more preferably at least 25 percent by weight. Also, the polyisocyanate curing agent is typically used in conjunction with the active hydrogen group-containing polymer in an amount of less than 50 percent by weight, and preferably less than 40 percent by weight, based on weight of total resin solids of (a) and (b). The polyisocyanate curing agent may be present in the thermosetting composition of the present invention in an amount ranging between any combination of these values, inclusive of the recited values.

[0151] The thermosetting compositions of the present invention are in the form of an aqueous dispersion. The term "dispersion" is believed to be a two-phase transparent, translucent or opaque resinous system in which the resin is in

the dispersed phase and the water is in the continuous phase. The average particle size of the resinous phase is generally less than 1.0 and usually less than 0.5 microns, preferably less than 0.15 micron.

[0152] The concentration of the resinous phase in the aqueous medium is at least 1 and usually from about 2 to about 60 percent by weight based on total weight of the aqueous dispersion. When the compositions of the present invention are in the form of resin concentrates, they generally have a resin solids content of about 20 to about 60 percent by weight based on weight of the aqueous dispersion.

[0153] The thermosetting compositions of the invention are typically in the form of electrodeposition baths which are usually supplied as two components: (1) a clear resin feed, which includes generally the active hydrogen-containing polymer which contains onium salt groups, i.e., the main film-forming polymer, the curing agent, and any additional water-dispersible, non-pigmented components; and (2) a pigment paste, which generally includes one or more pigments, a water-dispersible grind resin which can be the same or different from the main film-forming polymer, and, optionally, additives such as wetting or dispersing aids. Electrodeposition bath components (1) and (2) are dispersed in an aqueous medium which comprises water and, usually, coalescing solvents. Alternatively, the electrodeposition bath may be supplied as a one-component system which contains the main film-forming polymer, the curing agent, the pigment paste and any optional additives in one package. The one-component system is dispersed in an aqueous medium as described above.

[0154] The electrodeposition bath of the present invention has a resin solids content usually within the range of about 5 to 25 percent by weight based on total weight of the electrodeposition bath.

[0155] As aforementioned, besides water, the aqueous medium may contain a coalescing solvent. Useful coalescing solvents include hydrocarbons, alcohols, esters, ethers and ketones. The preferred coalescing solvents include alcohols, polyols and ketones. Specific coalescing solvents include isopropanol, butanol, 2-ethylhexanol, isophorone, 2-methoxy-pentanone, ethylene and propylene glycol and the monoethyl, monobutyl and monohexyl ethers of ethylene or propylene glycol. The amount of coalescing solvent is generally between about 0.01 and 25 percent and when used, preferably from about 0.05 to about 5 percent by weight based on total weight of the aqueous medium.

[0156] As discussed above, a pigment composition and, if desired, various additives such as surfactants, wetting agents or catalyst can be included in the dispersion. The pigment composition may be of the conventional type comprising pigments, for example, iron oxides, strontium chromate, carbon black, coal dust, titanium dioxide, talc, barium sulfate, as well as color pigments such as cadmium yellow, cadmium red, chromium yellow, and the like. The pigment content of the dispersion is usually expressed as a pigment-to-resin ratio. In the practice of the invention, when pigment is employed, the pigment-to-resin ratio is usually within the range of about 0.02: 1/1:1. The other additives mentioned above are usually in the dispersion in amounts of about 0.01 to 3 percent by weight based on weight of resin solids.

[0157] The thermosetting compositions of the present invention can be applied by electrodeposition to a variety of electroconductive substrates especially metals such as untreated steel, galvanized steel, aluminum, copper, magnesium and conductive carbon coated materials. The applied voltage for electrodeposition may be varied and can be, for example, as low as 1 volt to as high as several thousand volts, but typically between 25 and 500 volts. The current density is usually between 0.5 ampere and 5 amperes per square foot and tends to decrease during electrodeposition indicating the formation of an insulating film.

[0158] After the coating has been applied by electrodeposition, it is cured usually by baking at elevated temperatures such as about 90°C to about 260°C for about 1 to about 40 minutes.

[0159] The present invention is more particularly described in the following examples, which are intended to be illustrative only, since numerous modifications and variations therein will be apparent to those skilled in the art. Unless otherwise specified, all parts and percentages are by weight.

EXAMPLE 1:

[0160] A solution of 2,2'-azobis(2-methylbutyronitrile) (available as Vazo 67 from E.I. du Pont de Nemours and Company, Wilmington, DE) in toluene was heated to 90°C for three hours to produce the denitrogenated iniferter 2,3-dimethyl-2,3-dicyanobutane (DDCB).

EXAMPLE 2-4:

[0161] The 2,2'-azobis(2-methylbutyronitrile) (Vazo-67) was added to toluene, sparged with nitrogen for 15 minutes and heated to 80°C over a period of two hours to form DDCB. Each monomer charge was added over a 30 minute period and then held at the specified temperature for the specified period of time. Molecular weight measurements were made at appropriate intervals to determine whether the monomers were polymerizing into the quasi-living polymer. The details appear in Table 1.

Table 1

	Example 2	Example 3	Example 4
Vazo 67	15g	0.20g	40g
Toluene	300g	5.0ml	300g
Monomer 1	IBMA ² , 180g Toluene, 200g	VAc, 5ml	IBMA ² , 200g GHA ¹ , 35g
Temp./Time	80°C, 2 hrs.	70°C, 11 hrs.	80°C, 2 hrs.
Monomer 2	HPMA ³ , 120g		EHMA ⁴ , 250g
Temp./Time	80°C, 2 hrs.		80°C, 2 hrs.
GPC ⁵ Mw/PD ⁶	14,266/1.69	32,636/1.67	12,679/1.93
Time Interval	2.5 hrs.	4 hrs.	2.5 hrs.
GPC ⁵ Mw/PD ⁶	15,260/1.80	33,865/1.61	19,985/1.74
Time Interval	5 hrs.	11 hrs.	5 hrs.
¹ glycidylmethacrylate ² isobutylmethacrylate ³ hydroxypropylmethacrylate ⁴ 2-ethylhexylmethacrylate ⁵ Gel Permeation Chromatography using polystyrene standards ⁶ Polydispersity Index = Mw/Mn			

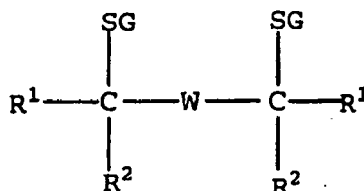
[0162] The data demonstrate the efficacy of the monofunctional iniferters of the present invention as well as the preparation of both homopolymers and block copolymers. The increase in molecular weight after the addition of the second monomer demonstrates its incorporation into the block copolymer. The unimodal nature of the GPC curves in each case also verifies block copolymer formation as two homopolymers would appear as a bi- or multi-modal distribution.

[0163] The present invention has been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as and to the extent that they are included in the accompanying claims.

Claims

1. A controlled radical polymerization process comprising the steps of:

(a) adding a compound capable of forming a carbon centered radical, which is able to initiate free radical polymerization, having the general structures :



wherein R¹ is selected from the group consisting of C₁-C₂₀ alkyl, cyclic, heterocyclic, alkynol, or aryl; R² is selected from the group consisting of H and C₁-C₄ alkyl; SG is a radical stabilizing group; and W is selected from the group consisting of a - C-C- bond and a group that can decompose to form two residues containing carbon centered radicals; to a solvent, forming a solution, which is substantially free of oxygen;

(b) heating the solution to a temperature 20°C to 250°C;

(c) adding a first monomer composition comprising one or more ethylenically unsaturated monomers to the solution containing the carbon centered radical residues; and

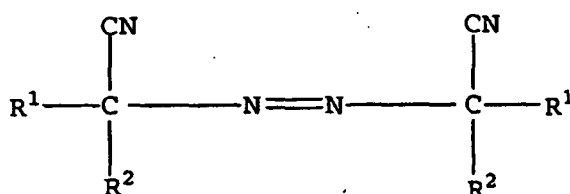
(d) polymerizing the first monomer composition to form a quasi-living polymer.

2. The controlled radical polymerization process of claim 1, wherein the polymer is a copolymer and further comprises the steps of:

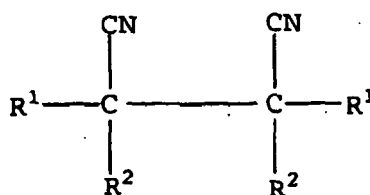
(e) adding a second monomer composition comprising one or more ethylenically unsaturated monomers, which is different than the first monomer composition, to the quasi-living polymer solution; and
(f) polymerizing the second monomer composition.

3. The controlled radical polymerization process of claim 1, wherein the radical stabilizing group is selected from the group consisting of nitrile, ester, amide, nitro, aryl and halide.

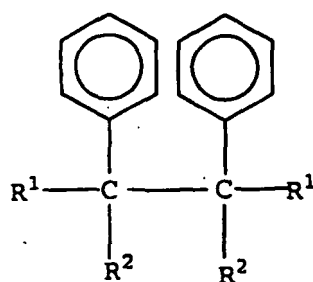
4. The controlled radical polymerization process of claim 1, wherein the compound capable of forming a carbon centered radical is selected from the group consisting of an azobisalkylnitrile having the general structure:



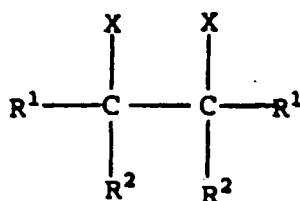
a bisalkylnitrile having the general structure:



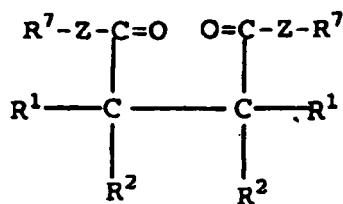
a bisphenylalkane having the following structure:



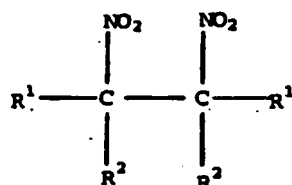
a bisalkolalkane having the following structures



a substituted biscoxyalkane having the following structure :

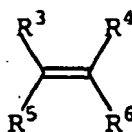


and a bisnitroalkane having the following structure:



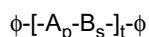
wherein R^1 and R^2 are independently selected from the group consisting of $\text{C}_1\text{-C}_{20}$ alkyl, cyclic, heterocyclic and alkynol; R^7 is selected from the group consisting of H, $\text{C}_1\text{-C}_{20}$ alkyl, cyclic, heterocyclic, alkynol and aryl; Z is selected from the group consisting of O and NH; and X is a halogen.

5. The controlled radical polymerization process of claim 4, wherein the 2-2'-azobisalkylnitrile is selected from the group consisting of 4-4'-azobis(4-cyanovaleric acid), 1-1'-azobiscyclohexanecarbonitrile), 1-1'-azobis(N-N-dimethylformamide, 2-2'-azobisisobutyronitrile, 2-2'-azobis(2-methylpropionamide) dihydrochloride, 2-2'-azobis(2-methylbutyronitrile), 2-2'-azobis(propionitrile), 2-2'-azobis(2,4-dimethylvaleronitrile) and 2-2'-azobis(valeronitrile).
6. The controlled radical polymerization process of any of the preceding claims, wherein the temperature is from 50°C to 200°C
7. The controlled radical polymerization process of any of the preceding claims, wherein the ethylenically unsaturated monomers are of the general formula :



wherein R^3 , R^4 and R^6 are independently selected from the group consisting of H, halogen, CN, CF_3 , straight or branched alkyl of 1 to 20 carbon atoms, aryl, unsaturated straight or branched alkenyl or alkynyl of 2 to 10 carbon atoms, unsaturated straight or branched alkenyl of 2 to 6 carbon atoms substituted with a halogen, $\text{C}_3\text{-C}_8$ cycloalkyl, heterocyclyl and phenyl; R^5 is selected from the group consisting of H, halogen, $\text{C}_3\text{-C}_8$ cycloalkyl, heterocyclyl and phenyl; R^5 is selected from the group consisting of H, halogen, $\text{C}_1\text{-C}_6$ alkyl, CN, COOR^8 , wherein R^8 is selected from the group consisting of H, an alkali metal, a $\text{C}_1\text{-C}_6$ alkyl group and aryl.

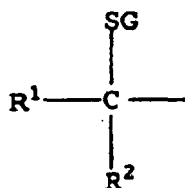
8. The controlled radical polymerization process of claim 7, wherein the ethylenically unsaturated monomers are alkyl (meth)acrylates.
9. A non-random copolymer of the following general formula:



wherein:

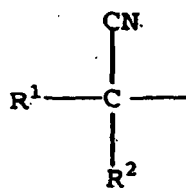
- a) A and B are different compositions of ethylenically unsaturated monomers,
- b) p is an integer from 1 to 1,000;
- c) s is an integer from 1 to 1,000;
- d) t is an integer from 1 to 100; and
- e) ϕ is a residue from a carbon centered radical capable of initiating free radical polymerization.

10. The nonrandom copolymer of claim 9, wherein the residue ϕ has the general formula :

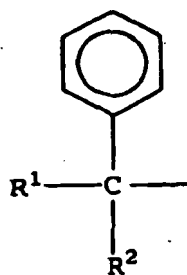


wherein R^1 is selected from the group consisting of C_1 - C_{20} alkyl, cyclic, heterocyclic, alkynol, or aryl; R^2 is selected from the group consisting of H and C_1 - C_4 alkyl and SG is a radical stabilizing group.

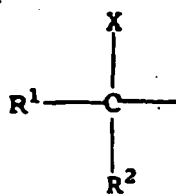
11. The non-random copolymer of claim 9, wherein the residue ϕ is selected from the group consisting of a residue having the general structure:



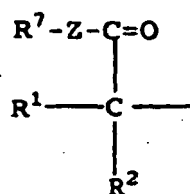
a residue having the following structure :



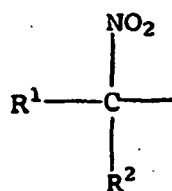
a residue having the following structure :



a substituted residue having the following structure :

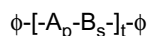


and a residue having the following structure:



wherein R¹ and R² are independently selected from the group consisting of C₁-C₂₀ alkyl, cyclic, heterocyclic and alkynol; R⁷ is selected from the group consisting of H, C₁-C₂₀ alkyl, cyclic, heterocyclic, alkynol, and aryl; Z is selected from the group consisting of O and NH; and X is a halide.

12. The non-random copolymer of claim 10, wherein the residue ϕ is selected from the group consisting of 4-cyanovaleric acid, cyclohexanecarbonitrile, N,N-dimethylformamide, isobutyronitrile, 2-methylpropionamide, 2-2-methylbutyronitrile, propionitrile, 2,4-dimethylvaleronitrile and valeronitrile.
13. The non-random copolymer of any of claims 9 - 12, wherein the ethylenically unsaturated monomers are defined as in any of claims 7 and 8.
14. The non-random copolymer of any of claims 9 - 13 having a number average molecular weight of from 500 to 1,000,000 as measured by gel permeation chromatography using polystyrene standards.
15. The non-random copolymer of any of claims 9 - 14 having a polydispersity index of less than 2.5.
16. A thermosetting composition comprising a co-reactable solid, particulate mixture of:
 - (a) a reactant having at least two functional groups; and
 - (b) a non-random copolymer of the following general formula:



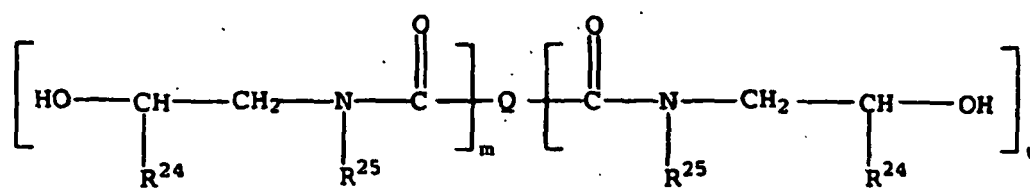
wherein:

- 1) A and B are different compositions of ethylenically unsaturated monomers, wherein B includes functional monomers having a functional group reactive with the functional groups of the reactant (a);
- 2) p is an integer from 1 to 1,000;
- 3) s is an integer from 1 to 1,000;
- 4) t is an integer from 1 to 100; and
- 5) ϕ is a residue from a carbon centered radical capable of initiating free radical polymerization.

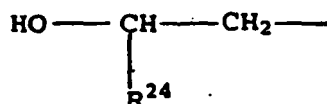
17. A thermosetting composition comprising

- a) a crosslinking agent having at least two functional groups; and
- b) a non-gelled, non-random copolymer as defined in claim 16.

18. The thermosetting composition of any of claims 16 and 17, wherein the functional groups of the reactant (a) are selected from the group consisting of epoxy, oxirane, carboxylic acid, hydroxy, polyol, isocyanate, capped isocyanate, amine, aminoplast and beta-hydroxyalkylamide; the functional groups of the non-random copolymer (b) are selected from the group consisting of epoxy, oxirane, carboxylic acid, hydroxy, amide, oxazoline, aceto acetate, isocyanate, and carbamate; and, wherein the functional groups of the reactant (a) are different than those in the non-random copolymer (b).
5
19. The thermosetting composition of claim 18, wherein the functional group of monomer composition B of the non-random copolymer (b) is hydroxy and the functional group of the reactant in (a) is a capped polyisocyanate, wherein the capping group of the capped polyisocyanate crosslinking agent is selected from the group consisting of hydroxy functional compounds, 1H-azoles, lactams, ketoximes and mixtures thereof.
10
20. The thermosetting composition of claim 18, wherein the capping group is selected from the group consisting of phenol, p-hydroxy methylbenzoate, 1H-1,2,4-triazole, 1H-2,5-dimethyl pyrazole, 2-propanone oxime, 2-butanone oxime, cyclohexanone oxime, e-caprolactam and mixtures thereof.
15
21. The thermosetting composition of claim 18, wherein the polyisocyanate of said capped polyisocyanate crosslinking agent is selected from the group consisting of 1,6-hexamethylene diisocyanate, cyclohexane diisocyanate, α,α' -xylylene diisocyanate, $\alpha,\alpha,\alpha',\alpha'$ -tetramethylxylylene diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 2,4,4-trimethyl hexamethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, diisocyanato-dicyclohexylmethane, dimers of said polyisocyanates, trimers of said polyisocyanates and mixtures thereof.
20
22. The thermosetting composition of claim 19 wherein the hydroxy functional polymer has a hydroxy equivalent weight of from 100 to 10,000 grams/equivalent.
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23. The thermosetting composition of claim 18, wherein A is derived from at least one of alkyl (meth)acrylates having from 1 to 20 carbon atoms in the alkyl group, vinyl aromatic monomers, vinyl halides, vinyl esters of carboxylic acids and olefins, and B is derived from hydroxyalkyl (meth)acrylates having from 1 to 20 carbon atoms in the alkyl group.
24. The thermosetting composition of claim 19, wherein the equivalent ratio of isocyanate equivalents in said capped polyisocyanate crosslinking agent (a) to hydroxy equivalents in said hydroxy functional polymer (b) is within the range of 1:3 to 3:1.
30
25. The thermosetting composition of claim 24, wherein said capped polyisocyanate crosslinking agent is present in an amount of from 1 to 45 percent by weight, based on total weight of resin solids, and said hydroxy functional polymer is present in an amount of from 55 to 99 percent by weight, based on total weight of resin solids.
35
26. The thermosetting composition of any of claims 16 and 17, wherein monomer composition B of the non-random copolymer (b) includes oxirane functional ethylenically unsaturated radically polymerizable monomers and the reactant (a) is a carboxylic functional co-reactant having from 4 to 20 carbon atoms.
40
27. The thermosetting composition of claim 26 wherein the carboxylic acid reactant is selected from the group consisting of dodecanedioic acid, azelaic acid, adipic acid, 1,6-hexanedioic acid, succinic acid, pimelic acid, sebacic acid, maleic acid, citric acid, itaconic acid, aconitic acid and mixtures thereof.
45
28. The thermosetting composition of claim 27 further comprising a second polycarboxylic acid functional material selected from the group consisting of C_4 - C_{20} aliphatic carboxylic acids, polymeric polyanhydrides, polyesters, polyurethanes and mixtures thereof.
29. The thermosetting composition of any of claims 16 and 17, wherein monomer composition B of the non-random copolymer (b) includes carboxylic functional ethylenically unsaturated radically polymerizable monomers and the reactant (a) is a beta-hydroxyalkylamide.
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30. The thermosetting composition of claim 29, wherein the beta-hydroxyalkylamide is represented by the following formula:
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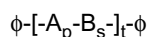
wherein R^{24} is H or $\text{C}_1\text{-C}_5$ alkyl; R^{25} is H, $\text{C}_1\text{-C}_5$ alkyl or



for which R^{24} is as described above, Q is a chemical bond or monovalent or polyvalent organic radical derived from saturated, unsaturated or aromatic hydrocarbon radicals including substituted hydrocarbon radicals containing from 2 to 20 carbon atoms, m is 1 or 2, t is from 0 to 2, and $m + t$ is at least 2.

31. The thermosetting composition of any of claims 16-30, wherein the non-random polymer is selected from the group consisting of linear polymers, branched polymers, hyperbranched polymers, star polymers, graft polymers and mixtures thereof.
32. The thermosetting composition of any of claims 16-31, wherein the non-random polymer has a number average molecular weight of from 500 to 16,000, and a polydispersity index of less than 2.5.
33. The thermosetting composition of any of claims 16-32, wherein the ethylenically unsaturated monomers of monomer composition A are defined as in any of claims 7 and 8.
34. A thermosetting composition comprising a resinous phase dispersed in an aqueous medium, said resinous phase comprising the following components:

(a) an ungelled, non-random copolymer of the following general formula:



wherein:

- (1) A and B are different compositions of ethylenically unsaturated monomers, with B including functional monomers with a functional group selected from the group consisting of active hydrogen groups and onium salt groups;
- (2) p is an integer from 1 to 1,000;
- (3) s is an integer from 1 to 1,000;
- (4) t is an integer from 1 to 100; and
- (5) ϕ is a residue from a carbon centered radical capable of initiating free radical polymerization; and

(b) a curing agent having at least two functional groups which are reactive with the active hydrogen groups of (a).

35. The thermosetting composition of claim 34, wherein the active hydrogen group-containing polymer has a number average molecular weight in the range of from 1,000 to 30,000.
36. The thermosetting composition of claim 34, wherein the polymer has an onium salt group equivalent weight of from 1,000 to 15,000 grams/equivalent.
37. The thermosetting composition of claim 34, wherein A is a residue derived from at least one of vinyl monomers,

allylic monomers, and olefins.

38. The thermosetting composition of claim 34, wherein A is derived from at least one of alkyl (meth)acrylates having 1 to 20 carbon atoms in the alkyl group, vinyl aromatic monomers and olefins.

39. The thermosetting composition of claim 34, wherein the active hydrogen groups of monomer composition B are derived from at least one of hydroxy-alkyl esters of (meth)acrylic acid containing from 1 to 4 carbon atoms in the hydroxy alkyl group.

40. The thermosetting composition of claim 34, wherein the active hydrogen groups of monomer composition B are derived from at least one of hydroxy-ethyl (meth)acrylate, and hydroxy-propyl (meth)acrylate.

41. The thermosetting composition of claim 34, wherein the onium salt of monomer composition B are selected from at least one of the class consisting of quaternary ammonium salts and ternary sulfonium salts.

42. The thermosetting composition of claim 34, wherein the non-random polymer further comprises segments of monomer composition G, which is derived from at least one epoxy group-containing ethylenically unsaturated monomer which after polymerization has been post-reacted with an amine acid salt.

43. The thermosetting composition of claim 42, wherein G is derived from at least one epoxy group-containing monomer which after polymerization has been post-reacted with a sulfide in the presence of an acid.

44. The thermosetting composition of claim 42, wherein the active hydrogen group-containing polymer is a substantially linear polymer having a number average molecular weight in the range of from 1,000 to 30,000, and wherein G is derived from at least one epoxy group-containing monomer which after polymerization has been post-reacted with an amine acid salt; B is derived from at least one hydroxy-alkyl (meth)acrylate having 1 to 4 carbon atoms in the alkyl group; and A is derived from at least one of (meth)acrylate monomers, vinyl aromatic monomers, and olefins.

45. The thermosetting composition of claim 44, wherein the polymer has an onium salt group equivalent weight in the range of from 1,000 to 15,000 grams/equivalent.

46. The thermosetting composition of claim 44, wherein the polymer, prior to onium salt group formation, has a polydispersity index of less than 2.5.

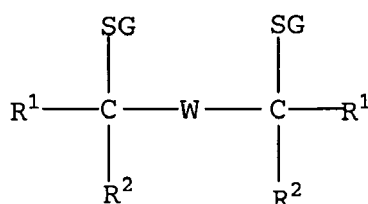
47. The thermosetting composition of any of claims 34 - 46, wherein component (a) is present in an amount ranging from 25 to 99 weight percent, and component (b) is present in an amount ranging from 1 to 75 weight percent, wherein the weight percentages are based on the total weight of (a) and (b).

48. The thermosetting composition of any of claims 16-47, wherein the residue ϕ is defined as in any of claims 10 - 12.

Patentansprüche

1. Kontrollierter radikalischer Polymerisationsprozess, umfassend die Schritte:

(a) Zugabe einer Verbindung, die in der Lage ist, ein kohlenstoffzentriertes Radikal zu bilden, das in der Lage ist, eine radikalische Polymerisation zu initiieren, mit der allgemeinen Struktur:



worin R^1 ausgewählt ist aus der Gruppe bestehend aus C_1 - bis C_{20} -Alkyl, einer cyclischen Gruppe, einer heterocyclischen Gruppe, Alkinol oder Aryl, R^2 ausgewählt ist aus der Gruppe bestehend aus H und C_1 - bis C_4 -Alkyl, SG eine Radikal stabilisierende Gruppe ist und W ausgewählt ist aus der Gruppe bestehend aus einer C-C-Bindung und einer Gruppe, die sich zersetzen kann, um zwei Reste zu bilden, die kohlenstoffzentrierte Radikale enthalten, zu einem Lösungsmittel, wodurch eine Lösung gebildet wird, die im Wesentlichen frei von Sauerstoff ist,

(b) Erwärmen der Lösung auf eine Temperatur von 20°C bis 250°C,

(c) Zugabe einer ersten Monomerzusammensetzung, die ein oder mehrere ethylenisch ungesättigte Monomere enthält, zu der Lösung, die die kohlenstoffzentrierten Radikalreste enthält, und

(d) Polymerisieren der ersten Monomerzusammensetzung, um ein quasi-lebendes Polymer zu bilden.

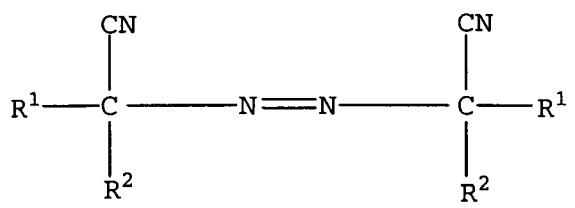
2. Kontrolliertes radikalisches Polymerisationsverfahren nach Anspruch 1, wobei das Polymer ein Copolymer ist und wobei das Verfahren zusätzlich die Schritte enthält:

(e) Zugabe einer zweiten Monomerzusammensetzung, die ein oder mehrere ethylenisch ungesättigte Monomere enthält, und sich von der ersten Monomerzusammensetzung unterscheidet, zu der Lösung des quasi-lebenden Polymers und

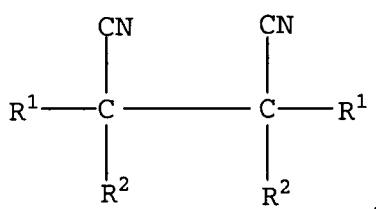
(f) Polymerisieren der zweiten Monomerzusammensetzung.

3. Kontrolliertes radikalisches Polymerisationsverfahren nach Anspruch 1, wobei die Radikal stabilisierende Gruppe ausgewählt ist aus der Gruppe bestehend aus Nitril, Ester, Amid, Nitro, Aryl und Halogenid.

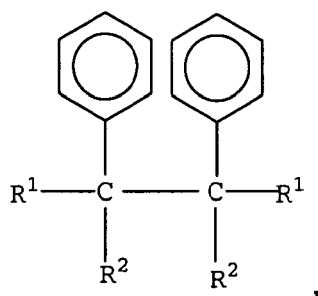
4. Kontrolliertes radikalisches Polymerisationsverfahren nach Anspruch 1, wobei die Verbindung, die in der Lage ist, ein kohlenstoffzentriertes Radikal zu bilden, ausgewählt ist aus der Gruppe bestehend aus einem Azobisalkylnitril mit der folgenden allgemeinen Struktur:



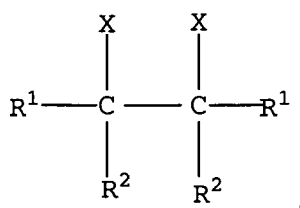
einem Bisalkylnitril mit der allgemeinen Struktur:



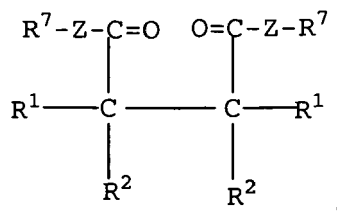
einem Bisphenylalkan mit der folgenden Struktur:



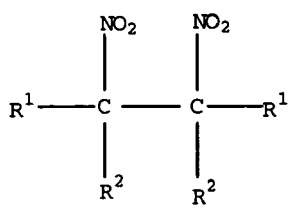
einem Bishalogenalkan mit der folgenden Struktur:



einem substituiertem Biscarboxyalkan mit der folgenden Struktur:



und einem Bisnitroalkan mit der folgenden Struktur:

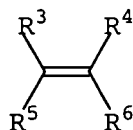


worin R^1 und R^2 unabhängig voneinander ausgewählt sind aus der Gruppe bestehend aus C_1 - bis C_{20} -Alkyl, einer cyclischen Gruppe, einer heterocyclischen Gruppe und Alkinol, R^7 ausgewählt ist aus der Gruppe bestehend aus H, C_1 - bis C_{20} -Alkyl, einer cyclischen Gruppe, einer heterocyclischen Gruppe, Alkinol und Aryl, Z ausgewählt ist aus der Gruppe bestehend aus O und NH und X ein Halogenid ist.

5. Kontrolliertes radikalisches Polymerisationsverfahren nach Anspruch 4, wobei das 2-2'-Azobisalkylnitril ausgewählt ist aus der Gruppe bestehend aus 4-4'-Azobis(4-cyanovaleriansäure), 1-1'-Azobiscyclohexancarbonitril, 1-1'-Azobis(N,N-dimethylformamid), 2-2'-Azobisisobutyronitril, 2-2'-Azobis(2-methylpropionamidin)dihydrochlorid, 2-2'-Azobis(2-methylbutyronitril), 2-2'-Azobis(propionitril), 2-2'-Azobis(2,4-dimethylvaleronitril) und 2-2'-Azobis(valeronitril).

6. Kontrolliertes radikalisches Polymerisationsverfahren nach einem der vorstehenden Ansprüche, wobei die Temperatur 50°C bis 200°C beträgt.

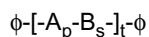
7. Kontrolliertes radikalisches Polymerisationsverfahren nach einem der vorstehenden Ansprüche, wobei die ethylenisch ungesättigten Monomere die folgende allgemeine Formel aufweisen:



worin R³, R⁴ und R⁶ unabhängig voneinander ausgewählt sind aus der Gruppe bestehend aus H, Halogen, CN, CF₃, geradkettigem oder verzweigtem Alkyl mit 1 bis 20 Kohlenstoffatomen, Aryl, ungesättigtem geradkettigem oder verzweigtem Alkenyl oder Alkynyl mit 2 bis 10 Kohlenstoffatomen, ungesättigtem geradkettigem oder verzweigtem Alkenyl mit 2 bis 6 Kohlenstoffatomen, das mit einem Halogen substituiert ist, C₃- bis C₈-Cycloalkyl, einer heterocyclischen Gruppe und Phenyl, R⁵ ausgewählt ist aus der Gruppe bestehend aus H, Halogen, C₃- bis C₈-Cycloalkyl, einer heterocyclischen Gruppe und Phenyl, R⁶ ausgewählt ist aus der Gruppe bestehend aus H, Halogen, C₁- bis C₆-Alkyl, CN, COOR⁸, worin R⁸ ausgewählt ist aus der Gruppe bestehend aus H, einem Alkalimetall, einer C₁- bis C₆-Alkylgruppe und Aryl.

8. Kontrolliertes radikalisches Polymerisationsverfahren nach Anspruch 7, wobei die ethylenisch ungesättigten Monomere Alkyl(meth)acrylate sind.

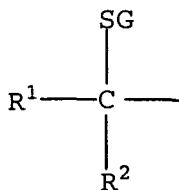
9. Ein nichtstatistisches Copolymer der folgenden allgemeinen Formel:



worin:

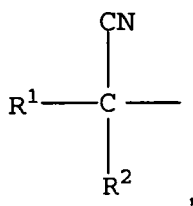
- a) A und B unterschiedliche Zusammensetzungen von ethylenisch ungesättigten Monomeren sind,
- b) p eine ganze Zahl von 1 bis 1.000 ist,
- c) s eine ganze Zahl von 1 bis 1.000 ist,
- d) t eine ganze Zahl von 1 bis 100 ist und
- e) ϕ ein Rest von einem kohlenstoffzentrierten Radikal ist, das in der Lage ist, eine Radikalpolymerisation zu initiieren.

10. Nichtstatistisches Copolymer nach Anspruch 9, wobei der Rest ϕ die allgemeine Formel aufweist:

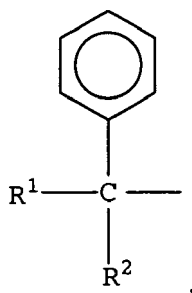


worin R¹ ausgewählt ist aus der Gruppe bestehend aus C₁- bis C₂₀-Alkyl, einer cyclischen Gruppe, einer heterocyclischen Gruppe, Alkinol oder Aryl, R² ausgewählt ist aus der Gruppe bestehend aus H und C₁- bis C₄-Alkyl und SG eine Radikal stabilisierende Gruppe ist.

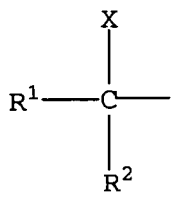
11. Nichtstatistisches Copolymer nach Anspruch 9, wobei der Rest ϕ ausgewählt ist aus der Gruppe bestehend aus einem Rest mit der allgemeinen Struktur:



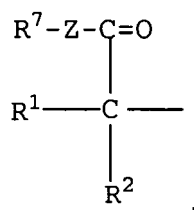
einem Rest mit der folgenden Struktur:



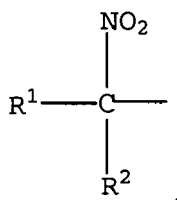
einem Rest mit der folgenden Struktur:



einem substituierten Rest mit der folgenden Struktur:



und einem Rest mit der folgenden Struktur:



worin R^1 and R^2 unabhängig voneinander ausgewählt sind aus der Gruppe bestehend aus C_1 - bis C_{20} -Alkyl, einer cyclischen Gruppe, einer heterocyclischen Gruppe und Alkinol, R^7 ausgewählt ist aus der Gruppe bestehend aus H, C_1 - bis C_{20} -Alkyl, einer cyclischen Gruppe, einer heterocyclischen Gruppe, Alkinol und Aryl, Z ausgewählt ist

aus der Gruppe bestehend aus O und NH und X ein Halogenid ist.

12. Nichtstatistisches Copolymer nach Anspruch 10, wobei der Rest ϕ ausgewählt ist aus der Gruppe bestehend aus 4-Cyanovaleriansäure, Cyclohexancarboxitril, N,N-Dimethylformamid, Isobutyronitril, 2-Methylpropionamidin, 2-2-Methylbutyronitril, Propionitril, 2,4-Dimethylvaleronitril und Valeronitril.

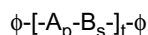
13. Nichtstatistisches Copolymer nach einem der Ansprüche 9 - 12, wobei die ethylenisch ungesättigten Monomere wie in einem der Ansprüche 7 und 8 definiert sind.

14. Nichtstatistisches Copolymer nach einem der Ansprüche 9 - 13 mit einem zahlenmittleren Molekulargewicht von 500 bis 1.000.000, gemessen durch Gelpermeationschromatographie unter Verwendung von Polystyrolstandards.

15. Nichtstatistisches Copolymer nach einem der Ansprüche 9 - 14 mit einem Polydispersitätsindex von kleiner als 2,5.

16. Wärmehärtende Zusammensetzung, enthaltend eine coreaktive feste teilchenförmige Mischung von:

- (a) einem Reaktanten mit wenigstens zwei funktionellen Gruppen und
- (b) einem nichtstatistischen Copolymer der folgenden allgemeinen Formel:



worin:

- 1) A und B unterschiedliche Zusammensetzungen von ethylenisch ungesättigten Monomeren sind, worin B funktionelle Monomere enthält, die eine funktionelle Gruppe aufweisen, die mit den funktionellen Gruppen des Reaktanten (a) reaktiv ist,
- 2) p eine ganze Zahl von 1 bis 1.000 ist,
- 3) s eine ganze Zahl von 1 bis 1.000 ist,
- 4) t eine ganze Zahl von 1 bis 100 ist und
- 5) ϕ ein Rest eines kohlenstoffzentrierten Radikals ist, das in der Lage ist, eine radikalische Polymerisation zu initiieren.

17. Wärmehärtende Zusammensetzung, enthaltend

- (a) ein Vernetzungsmittel mit wenigstens zwei funktionellen Gruppen und
- b) ein nichtgelientes nichtstatistisches Copolymer wie in Anspruch 16 definiert.

18. Wärmehärtende Zusammensetzung nach einem der Ansprüche 16 und 17, wobei die funktionellen Gruppen des Reaktanten (a) ausgewählt sind aus der Gruppe bestehend aus Epoxy, Oxiran, Carbonsäure, Hydroxy, Polyol, Isocyanat, verkapptem Isocyanat, Amin, Aminoplast und β -Hydroxyalkylamid, die funktionellen Gruppen des nichtstatistischen Copolymers (b) ausgewählt sind aus der Gruppe bestehend aus Epoxy, Oxiran, Carbonsäure, Hydroxy, Amid, Oxazolin, Acetoacetat, Isocyanat und Carbamat und wobei die funktionellen Gruppen des Reaktanten (a) sich von denen des nichtstatistischen Copolymers (b) unterscheiden.

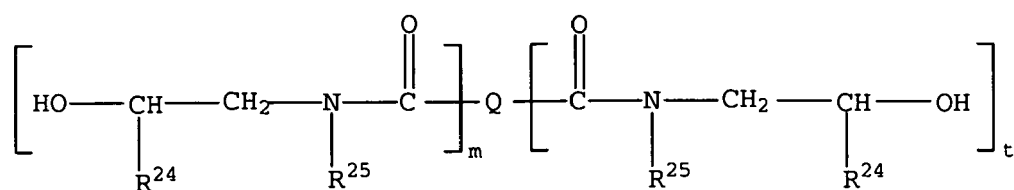
19. Wärmehärtende Zusammensetzung nach Anspruch 18, wobei die funktionelle Gruppe der Monomerzusammensetzung B des nichtstatistischen Copolymers (b) Hydroxy ist und die funktionelle Gruppe des Reaktanten (a) ein verkapptes Polyisocyanat ist, worin die Verkapppungsgruppe des verkappten Polyisocyanatvernetzungsmittels ausgewählt ist aus der Gruppe bestehend aus hydroxyfunktionellen Verbindungen, 1 H-Azolen, Lactamen, Ketoximen und Mischungen davon.

20. Wärmehärtende Zusammensetzung nach Anspruch 18, wobei die Verkapppungsgruppe ausgewählt ist aus der Gruppe bestehend aus Phenol, para-Hydroxymethylbenzoat, 1H-1,2,4-Triazol, 1H-2,5-Dimethylpyrazol, 2-Propanonoxim, 2-Butanonoxim, Cyclohexanonoxim, ϵ -Caprolactam und Mischungen davon.

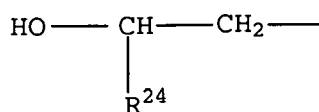
21. Wärmehärtende Zusammensetzung nach Anspruch 18, wobei das Polyisocyanat dieses verkappten Polyisocyanatvernetzungsmittels ausgewählt ist aus der Gruppe bestehend aus 1,6-Hexamethylen-diisocyanat, Cyclohexan-diisocyanat, α,α' -Xylylen-diisocyanat, $\alpha,\alpha,\alpha',\alpha'$ -Tetramethylxylylen-diisocyanat, 1-Isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexan, 2,4,4-Trimethylhexamethylen-diisocyanat, 2,2,4-Trimethylhexamethylen-diisocyanat, Di-

isocyanatodicyclohexylmethan, Dimeren dieser Polyisocyanate, Trimeren dieser Polyisocyanate und Mischungen davon.

22. Wärmehärtende Zusammensetzung nach Anspruch 19, wobei das hydroxyfunktionelle Polymer ein Hydroxyäquivalentgewicht von 100 bis 10.000 g/Äquivalent aufweist.
23. Wärmehärtende Zusammensetzung nach Anspruch 18, wobei A sich von wenigstens einem von Alkyl(meth)acrylaten mit 1 bis 20 Kohlenstoffatomen in der Alkylgruppe, aromatischen Vinylmonomeren, Vinylhalogeniden, Vinylestern von Carbonsäuren und Olefinen ableitet und B sich von Hydroxyalkyl(meth)acrylaten mit 1 bis 20 Kohlenstoffatomen in der Alkylgruppe ableitet.
24. Wärmehärtende Zusammensetzung nach Anspruch 19, wobei das Äquivalentverhältnis von Isocyanatäquivalenten in diesem verkappten Polyisocyanatvernetzungsmittels (a) zu Hydroxyäquivalenten in diesem hydroxyfunktionellen Polymer (b) im Bereich von 1:3 bis 3:1 liegt.
25. Wärmehärtende Zusammensetzung nach Anspruch 24, wobei dieses verkappte Polyisocyanatvernetzungsmittel in einer Menge von 1 bis 45 Gew.-%, bezogen auf das Gesamtgewicht von Harzfeststoffen, vorhanden ist und dieses hydroxyfunktionelle Polymer in einer Menge von 55 bis 99 Gew.-%, bezogen auf das Gesamtgewicht von Harzfeststoffen, vorhanden ist.
26. Wärmehärtende Zusammensetzung nach einem der Ansprüche 16 und 17, worin Monomerzusammensetzung B des nichtstatistischen Copolymers (b) oxiranfunktionelle ethylenisch ungesättigte radikalisch polymerisierbare Monomere enthält und der Reaktant (a) ein carbonsäurefunktioneller Coreaktant mit 4 bis 20 Kohlenstoffatomen ist.
27. Wärmehärtende Zusammensetzung nach Anspruch 26, wobei der Carbonsäurereaktant ausgewählt ist aus der Gruppe bestehend aus Dodecandicarbonsäure, Azelainsäure, Adipinsäure, 1,6-Hexandicarbonsäure, Bernsteinsäure, Pimelinsäure, Sebacinsäure, Maleinsäure, Zitronensäure, Itaconsäure, Aconitsäure und Mischungen davon.
28. Wärmehärtende Zusammensetzung nach Anspruch 27, die weiterhin ein zweites polycarbonsäurefunktionelles Material enthält, das ausgewählt ist aus der Gruppe bestehend aus C₄-bis C₂₀-aliphatischen Carbonsäuren, polymeren Polyanhydriden, Polyestern, Polyurethanen und Mischungen davon.
29. Wärmehärtende Zusammensetzung nach einem der Ansprüche 16 und 17, worin Monomerzusammensetzung B des nichtstatistischen Copolymers (b) carbonsäurefunktionelle ethylenisch ungesättigte radikalisch polymerisierbare Monomere enthält und der Reaktant (a) ein β-Hydroxyalkylamid ist.
30. Wärmehärtende Zusammensetzung nach Anspruch 29, wobei das β-Hydroxyalkylamid durch die folgende Formel wiedergegeben ist:



worin R²⁴ gleich H oder C₁- bis C₅-Alkyl ist, R²⁵ gleich H, C₁- bis C₅-Alkyl oder



ist, worin R²⁴ wie oben beschrieben ist, Q eine chemische Bindung oder ein einbindiger oder mehrbindiger organischer

Rest ist, der sich von gesättigten, ungesättigten oder aromatischen Kohlenwasserstoffresten einschließlich substituierten Kohlenwasserstoffresten mit 2 bis 20 Kohlenstoffatomen ableitet, m gleich 1 oder 2 ist, t von 0 bis 2 ist und m + t wenigstens 2 ist.

- 5 31. Wärmehärtende Zusammensetzung nach einem der Ansprüche 16 bis 30, worin das nichtstatistische Polymer ausgewählt ist aus der Gruppe bestehend aus linearen Polymeren, verzweigten Polymeren, hypervverzweigten Polymeren, Sternpolymeren, Pfropfpolymeren und Mischungen davon.
- 10 32. Wärmehärtende Zusammensetzung nach einem der Ansprüche 16 bis 31, worin das nichtstatistische Polymer ein zahlenmittleres Molekulargewicht von 500 bis 16.000 und einen Polydispersitätsindex von kleiner als 2,5 aufweist.
33. Wärmehärtende Zusammensetzung nach einem der Ansprüche 16 bis 32, wobei die ethylenisch ungesättigten Monomere der Monomerzusammensetzung A wie in einem der Ansprüche 7 und 8 definiert sind.
- 15 34. Wärmehärtende Zusammensetzung, enthaltend eine Harzphase, die in einem wässrigen Medium dispergiert ist, wobei diese Harzphase die folgenden Komponenten enthält:

(a) ein nichtgeliertes nichtstatistisches Copolymer der folgenden allgemeinen Formel:



worin:

- 25 1) A und B unterschiedliche Zusammensetzungen von ethylenisch ungesättigten Monomeren sind, worin B funktionelle Monomere mit einer funktionellen Gruppe, die ausgewählt ist aus der Gruppe bestehend aus aktiven Wasserstoffgruppen und Oniumsalzgruppen, enthält,
- 2) p eine ganze Zahl von 1 bis 1.000 ist,
- 3) s eine ganze Zahl von 1 bis 1.000 ist,
- 4) t eine ganze Zahl von 1 bis 100 ist und
- 30 5) ϕ ein Rest eines kohlenstoffzentrierten Radikals ist, das in der Lage ist, eine radikalische Polymerisation zu initiieren, und

(b) ein Härtungsmittel mit wenigstens zwei funktionellen Gruppen, die mit den aktiven Wasserstoffgruppen von (a) reaktiv sind.

- 35 35. Wärmehärtende Zusammensetzung nach Anspruch 34, wobei das aktive Wasserstoffgruppen enthaltende Polymer ein zahlenmittleres Molekulargewicht im Bereich von 1.000 bis 30.000 aufweist.
- 40 36. Wärmehärtende Zusammensetzung nach Anspruch 34, wobei das Polymer ein Oniumsalzgruppenäquivalentgewicht von 1.000 bis 15.000 g/Äquivalent aufweist.
37. Wärmehärtende Zusammensetzung nach Anspruch 34, wobei A ein Rest ist, der sich von wenigstens einem von Vinylmonomeren, allylischen Monomeren und Olefinen ableitet.
- 45 38. Wärmehärtende Zusammensetzung nach Anspruch 34, wobei A sich von wenigstens einem von Alkyl(meth)acrylaten mit 1 bis 20 Kohlenstoffatomen in der Alkylgruppe, aromatischen Vinylmonomeren und Olefinen ableitet.
39. Wärmehärtende Zusammensetzung nach Anspruch 34, wobei die aktiven Wasserstoffgruppen der Monomerzusammensetzung B sich von wenigstens einem Hydroxyalkylester von (Meth)acrylsäure mit 1 bis 4 Kohlenstoffatomen in der Hydroxyalkylgruppe ableiten.
- 50 40. Wärmehärtende Zusammensetzung nach Anspruch 34, wobei die aktiven Wasserstoffgruppen der Monomerzusammensetzung B sich von wenigstens einem von Hydroxyethyl(meth)acrylat und Hydroxypropyl(meth)acrylat ableiten.
- 55 41. Wärmehärtende Zusammensetzung nach Anspruch 34, wobei das Oniumsalz der Monomerzusammensetzung B ausgewählt ist aus wenigstens einem der Klasse bestehend aus quartären Ammoniumsalzen und ternären Sulfoniumsalzen.

42. Wärmehärtende Zusammensetzung nach Anspruch 34, wobei das nichtstatistische Polymer zusätzlich Segmente der Monomierzusammensetzung G enthält, die sich von wenigstens einem epoxygruppenhaltigen ethylenisch ungesättigten Monomer ableitet, das nach Polymerisation mit einem Säuresalz eines Amins umgesetzt worden ist.

43. Wärmehärtende Zusammensetzung nach Anspruch 42, wobei G sich von wenigstens einem epoxygruppenhaltigen Monomer ableitet, das nach Polymerisation mit einem Sulfid in Gegenwart einer Säure umgesetzt worden sind.

44. Wärmehärtende Zusammensetzung nach Anspruch 42, wobei das aktive Wasserstoffgruppen enthaltende Polymer ein im Wesentlichen lineares Polymer mit einem zahlenmittleres Molekulargewicht im Bereich von 1.000 bis 30.000 ist und worin

G sich von wenigstens einem epoxygruppenhaltigen Monomer ableitet, das nach der Polymerisation mit einem Säuresalz eines Amins umgesetzt worden ist,

B sich von wenigstens einem Hydroxyalkyl(meth)acrylat mit 1 bis 4 Kohlenstoffatomen in der Alkylgruppe ableitet und

A sich von wenigstens einem von (Meth)acrylatmonomeren, aromatischen Vinylmonomer und Olefinen ableitet.

45. Wärmehärtende Zusammensetzung nach Anspruch 44, wobei das Polymer ein Oniumsalzgruppenäquivalentgewicht im Bereich von 1.000 bis 15.000 g/Äquivalent aufweist.

46. Wärmehärtende Zusammensetzung nach Anspruch 44, wobei das Polymer vor der Oniumsalzgruppenbildung einen Polydispersitätsindex von kleiner als 2,5 aufweist.

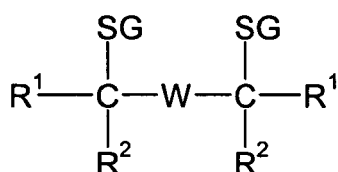
47. Wärmehärtende Zusammensetzung nach einem der Ansprüche 34-46, worin Komponente (a) in einer Menge im Bereich von 25 bis 99 Gew.-% und Komponente (b) in einer Menge im Bereich von 1 bis 75 Gew.-% vorhanden ist, wobei die Gewichtsprozentangaben sich auf das Gesamtgewicht von (a) und (b) beziehen.

48. Wärmehärtende Zusammensetzung nach einem der Ansprüche 16-47, worin der Rest ϕ wie in einem der Ansprüche 10-12 definiert ist.

Revendications

1. Procédé de polymérisation radicalaire contrôlée, comprenant les étapes consistant à :

(a) ajouter un composé capable de former un radical centré sur un carbone, qui est capable d'amorcer une polymérisation radicalaire, de structure générale :



dans laquelle R^1 est choisi dans l'ensemble constitué par les radicaux alkyle en C_1 - C_{20} , cycliques, hétérocycliques, alcynol, ou aryle ; R^2 est choisi dans l'ensemble constitué par H et les radicaux alkyle en C_1 - C_4 ; SG est un groupe de stabilisation radicalaire ; et W est choisi dans l'ensemble constitué par une liaison -C-C- et un groupe qui peut se décomposer pour former deux résidus contenant des radicaux centrés sur un carbone ; à un solvant, formant une solution, qui est pratiquement exempt d'oxygène ;

(b) chauffer la solution à une température de 20°C à 250°C ;

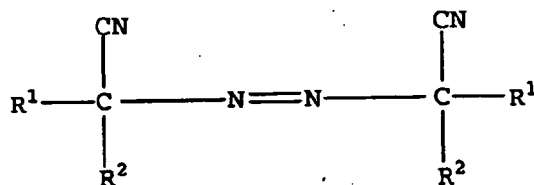
(c) ajouter une première composition de monomères, comprenant un ou plusieurs monomères à insaturation éthylénique, à la solution contenant les résidus radicalaires centrés sur un carbone ; et

(d) polymériser la première composition de monomères pour former un polymère quasi-vivant.

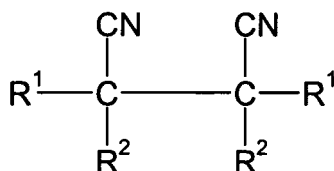
2. Procédé de polymérisation radicalaire contrôlée selon la revendication 1, dans lequel le polymère est un copolymère, et comprenant en outre les étapes consistant à :

(e) ajouter une deuxième composition de monomères, comprenant un ou plusieurs monomères à insaturation éthylénique, qui est différente de la première composition de monomères, à la solution de polymère quasi-vivant ; et
 (f) polymériser la deuxième composition de monomères.

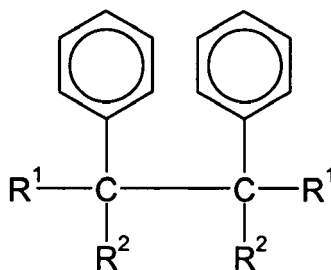
3. Procédé de polymérisation radicalaire contrôlée selon la revendication 1, dans lequel le groupe de stabilisation radicalaire est choisi dans l'ensemble constitué par les radicaux nitriles, ester, amide, nitro, aryle et halogénure.
4. Procédé de polymérisation radicalaire contrôlée selon la revendication 1, dans lequel le composé capable de former un radical centré sur un carbone est choisi dans l'ensemble constitué par un azobisalkylnitrile de structure générale :



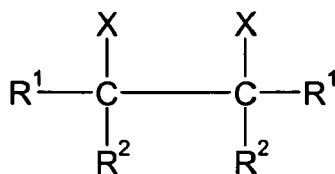
un bisalkylnitrile de structure générale :



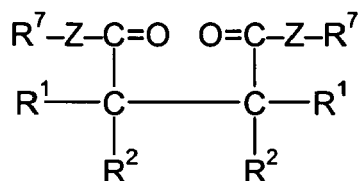
un bisphénylalcane de structure suivante :



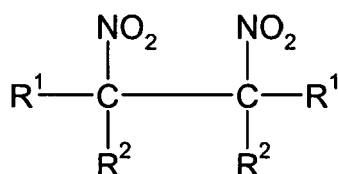
un bishalogénoalcane de structure suivante :



un biscarboxyalcane substitué de structure suivante :

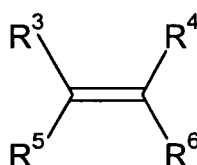


et un bisnitroalcane de structure suivante :



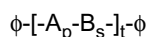
dans lesquels R^1 et R^2 sont indépendamment choisis dans l'ensemble constitué par les radicaux alkyle en C_1 - C_{20} , cycliques, hétérocycliques, et alcynol ; R^7 est choisi dans l'ensemble constitué par H et les radicaux alkyle en C_1 - C_{20} , cycliques, hétérocycliques, alcynol et aryle ; Z est choisi dans l'ensemble constitué par O et NH ; et X est un halogène.

5. Procédé de polymérisation radicalaire contrôlée selon la revendication 4, dans lequel le 2,2'-azobisalkylnitrile est choisi dans l'ensemble constitué par le 4,4'-azobis(acide 4-cyanovalérique), le 1,1'-azobis(cyclohexanecarbonitrile), le 1,1'-azobis(N,N-diméthylformamide), le 2,2'-azobis(isobutyronitrile), le dichlorhydrate de 2,2'-azobis(2-méthylpropionamidine), le 2,2'-azobis(2-méthylbutyronitrile), le 2,2'-azobis(propionitrile), le 2,2'-azobis(2,4-diméthylvaléronitrile) et le 2,2'-azobis(valéronitrile).
6. Procédé de polymérisation radicalaire contrôlée selon l'une quelconque des revendications précédentes, dans lequel la température est de 50°C à 200°C.
7. Procédé de polymérisation radicalaire contrôlée selon l'une quelconque des revendications précédentes, dans lequel les monomères à insaturation éthylénique répondent à la formule générale :



dans laquelle R^3 , R^4 et R^6 sont indépendamment choisis dans l'ensemble constitué par H, les halogènes et les radicaux CN, CF_3 , alkyle linéaires ou ramifiés ayant de 1 à 20 atomes de carbone, aryle, alcényle ou alcynyle insaturés linéaires ou ramifiés ayant de 2 à 10 atomes de carbone, alcényle insaturés linéaires ou ramifiés ayant de 2 à 6 atomes de carbone substitués par un halogène, cycloalkyle en C_3 - C_8 , hétérocyclyle et phényle ; R^5 est choisi dans l'ensemble constitué par H, les halogènes et les radicaux cycloalkyle en C_3 - C_8 , hétérocyclyle et phényle ; R^5 est choisi dans l'ensemble constitué par H, les halogènes et les radicaux alkyle en C_1 - C_6 , CN, COOR^8 où R^8 est choisi dans l'ensemble constitué par H, un métal alcalin, un groupe alkyle en C_1 - C_6 et aryle.

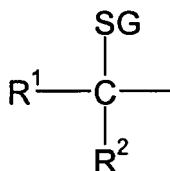
8. Procédé de polymérisation radicalaire contrôlée selon la revendication 7, dans lequel les monomères à insaturation éthylénique sont des (méth)acrylates d'alkyle.
9. Copolymère non aléatoire de formule générale suivante :



dans laquelle :

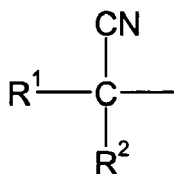
- a) A et B sont des compositions différentes de monomères à insaturation éthylénique ;
 b) p est un entier de 1 à 1000 ;
 c) s est un entier de 1 à 1000 ;
 d) t est un entier de 1 à 100 ; et
 e) ϕ est un résidu provenant d'un radical centré sur un carbone capable d'amorcer une polymérisation radicalaire.

10. Copolymère non aléatoire selon la revendication 9, dans lequel le résidu ϕ répond à la formule générale :

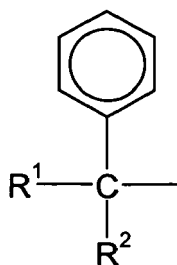


dans laquelle R^1 est choisi dans l'ensemble constitué par les radicaux alkyle en C_1 - C_{20} , cycliques, hétérocycliques, alcynol, et aryle ; R^2 est choisi dans l'ensemble constitué par H et les radicaux alkyle en C_1 - C_4 , et SG est un groupe de stabilisation radicalaire.

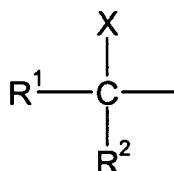
11. Copolymère non aléatoire selon la revendication 9, dans lequel le résidu ϕ est choisi dans l'ensemble constitué par un résidu de structure générale :



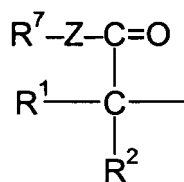
un résidu de structure suivante :



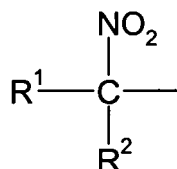
un résidu de structure suivante :



un résidu substitué de structure suivante :



et un résidu de structure suivante :



dans lesquels R^1 et R^2 sont indépendamment choisis dans l'ensemble constitué par les radicaux alkyle en C_1 - C_{20} , cycliques, hétérocycliques, et alcynol ; R^7 est choisi dans l'ensemble constitué par H et les radicaux alkyle en C_1 - C_{20} , cycliques, hétérocycliques, alcynol et aryle ; Z est choisi dans l'ensemble constitué par O et NH ; et X est un halogène.

12. Copolymère non aléatoire selon la revendication 10, dans lequel le résidu ϕ est choisi dans l'ensemble constitué par l'acide 4-cyanovalérique, le cyclohexane-carbonitrile, le N,N-diméthylformamide, l'isobutyronitrile, la 2-méthylpropionamidine, le 2,2-méthylbutyronitrile, le propionitrile, le 2,4-diméthylvaléronitrile et le valéronitrile.

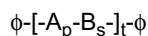
13. Copolymère non aléatoire selon l'une quelconque des revendications 9 à 12, dans lequel les monomères à insaturation éthylénique sont tels que définis dans l'une quelconque des revendications 7 et 8.

14. Copolymère non aléatoire selon l'une quelconque des revendications 9 à 13, ayant une masse moléculaire moyenne en nombre de 500 à 1 000 000 telle que mesurée par chromatographie par perméation sur gel utilisant des étalons de polystyrène.

15. Copolymère non aléatoire selon l'une quelconque des revendications 9 à 14, ayant un indice de polydispersité inférieur à 2,5.

16. Composition thermodurcissable comprenant un mélange particulaire solide pouvant co-réagir, constitué de :

- (a) un réactif ayant au moins deux groupes fonctionnels ; et
- (b) un copolymère non aléatoire de formule générale suivante :



dans laquelle :

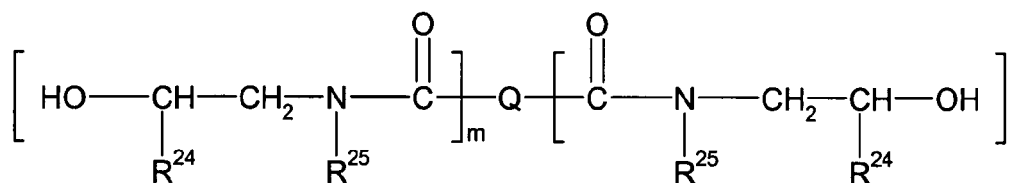
- 1) A et B sont des compositions différentes de monomères à insaturation éthylénique, où B contient des monomères fonctionnels ayant un groupe fonctionnel réactif vis-à-vis des groupes fonctionnels du réactif (a) ;
- 2) p est un entier de 1 à 1000 ;
- 3) s est un entier de 1 à 1000 ;
- 4) t est un entier de 1 à 100 ; et
- 5) ϕ est un résidu provenant d'un radical centré sur un carbone capable d'amorcer une polymérisation radicalaire.

17. Composition thermodurcissable comprenant :

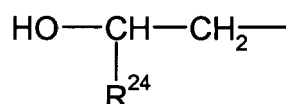
- a) un agent de réticulation ayant au moins deux groupes fonctionnels ; et
- b) un copolymère non statistique non gélifié tel que défini dans la revendication 16.

18. Composition thermodurcissable selon l'une quelconque des revendications 16 et 17, dans laquelle les groupes fonctionnels du réactif (a) sont choisis dans l'ensemble constitué par les radicaux époxy, oxirane, acide carboxylique, hydroxy, polyol, isocyanate, isocyanate coiffé, amine, aminoplaste et β -hydroxyalkylamide ; les groupes fonctionnels du copolymère non statistique (b) sont choisis dans l'ensemble constitué par les radicaux époxy, oxirane, acide carboxylique, hydroxy, amide, oxazoline, acétoacétate, isocyanate, et carbamate ; et dans laquelle les groupes fonctionnels du réactif (a) sont différents de ceux du copolymère non statistique (b).
19. Composition thermodurcissable selon la revendication 18, dans laquelle le groupe fonctionnel de la composition de monomères B du copolymère non statistique (b) est le groupe hydroxy et le groupe fonctionnel du réactif dans (a) est un polyisocyanate coiffé, où le groupe de coiffage de l'agent de réticulation à base de polyisocyanate coiffé est choisi dans l'ensemble constitué par les composés à fonctionnalité hydroxy, les 1H-azoles, les lactames, les cétoximes et leurs mélanges.
20. Composition thermodurcissable selon la revendication 18, dans laquelle le groupe de coiffage est choisi dans l'ensemble constitué par le phénol, le benzoate de p-hydroxyméthyle, le 1H-1,2,4-triazole, le 1H-2,5-diméthylpyrazole, la 2-propanone-oxime, la 2-butanone-oxime, la cyclohexanone-oxime, l' ϵ -caprolactame et leurs mélanges.
21. Composition thermodurcissable selon la revendication 18, dans laquelle le polyisocyanate dudit agent de réticulation à base de polyisocyanate coiffé est choisi dans l'ensemble constitué par le diisocyanate de 1,6-hexaméthylène, le diisocyanate de cyclohexane, le diisocyanate d' α,α' -xylylène, le diisocyanate d' $\alpha,\alpha,\alpha',\alpha'$ -tétraméthylxylène, le 1-isocyanato-3,3,5-triméthyl-5-isocyanatométhylcyclohexane, le diisocyanate de 2,4,4-triméthylhexaméthylène, le diisocyanate de 2,2,4-triméthylhexaméthylène, le diisocyanato-dicyclohexyl-méthane, les dimères desdits polyisocyanates, les trimères desdits polyisocyanates, et leurs mélanges.
22. Composition thermodurcissable selon la revendication 19, dans laquelle le polymère à fonctionnalité hydroxy a une masse d'équivalent hydroxy de 100 à 10 000 grammes / équivalent.
23. Composition thermodurcissable selon la revendication 18, dans laquelle A dérive d'au moins l'un parmi les (méth)acrylates d'alkyle ayant de 1 à 20 atomes de carbone dans le groupe alkyle, les monomères vinylaromatiques, les halogénures de vinyle, les esters vinyliques d'acides carboxyliques et les oléfines, et B dérive de (méth)acrylates d'hydroxyalkyle ayant de 1 à 20 atomes de carbone dans le groupe alkyle.
24. Composition thermodurcissable selon la revendication 19, dans laquelle le rapport équivalent des équivalents isocyanates dans ledit agent de réticulation à base de polyisocyanate coiffé (a) aux équivalents hydroxy dans ledit polymère à fonctionnalité hydroxy (b) est situé dans la plage allant de 1/3 à 3/1.
25. Composition thermodurcissable selon la revendication 24, dans laquelle ledit agent de réticulation à base de polyisocyanate coiffé est présent en une quantité de 1 à 45 % en poids, par rapport au poids total d'extrait sec de résine, et ledit polymère à fonctionnalité hydroxy est présent en une quantité de 55 à 99 % en poids, par rapport au poids total d'extrait sec de résine.
26. Composition thermodurcissable selon l'une quelconque des revendications 16 et 17, dans laquelle la composition de monomères B du copolymère non statistique (b) contient des monomères polymérisables par polymérisation radicalaire, à insaturation éthylénique, à fonctionnalité oxirane, et le réactif (a) est un co-réactif à fonctionnalité carboxylique ayant de 4 à 20 atomes de carbone.
27. Composition thermodurcissable selon la revendication 26, dans laquelle le réactif acide carboxylique est choisi dans le groupe constitué par l'acide dodécanedioïque, l'acide azélaïque, l'acide adipique, l'acide 1,6-hexanedioïque, l'acide succinique, l'acide pimélique, l'acide sébacique, l'acide maléique, l'acide citrique, l'acide itaconique, l'acide aconitique et leurs mélanges.
28. Composition thermodurcissable selon la revendication 27, comprenant en outre un deuxième matériau à fonctionnalité acide polycarboxylique choisi dans l'ensemble constitué par les acides carboxyliques aliphatiques en C_4 - C_{20} , les polyanhydrides polymères, les polyesters, les polyuréthanes et leurs mélanges.
29. Composition thermodurcissable selon l'une quelconque des revendications 16 et 17, dans laquelle la composition de monomères B du copolymère non statistique (b) contient des monomères polymérisables par polymérisation radicalaire, à insaturation éthylénique, à fonctionnalité carboxylique, et le réactif (a) est un β -hydroxyalkylamide.

30. Composition thermodurcissable selon la revendication 29, dans lequel le β -hydroxyalkylamide est représenté par la formule suivante :



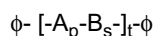
dans laquelle R^{24} est H ou un radical alkyle en $\text{C}_1\text{-C}_5$; R^{25} est H ou un radical alkyle en $\text{C}_1\text{-C}_5$ ou



où R^{24} est tel que décrit ci-dessus, Q est une liaison chimique ou un radical organique monovalent ou polyvalent dérivant de radicaux hydrocarbonés saturés, insaturés ou aromatiques, y compris les radicaux hydrocarbonés substitués contenant de 2 à 20 atomes de carbone, m vaut 1 ou 2, t vaut de 0 à 2, et m + t vaut au moins 2.

31. Composition thermodurcissable selon l'une quelconque des revendications 16 à 30, dans laquelle le polymère non aléatoire est choisi dans l'ensemble constitué par les polymères linéaires, les polymères ramifiés, les polymères hyper-ramifiés, les polymères en étoile, les polymères greffés et leurs mélanges.
32. Composition thermodurcissable selon l'une quelconque des revendications 16 à 31, dans laquelle le polymère non aléatoire a une masse moléculaire moyenne en nombre de 500 à 16 000 et un indice de polydispersité inférieur à 2,5.
33. Composition thermodurcissable selon l'une quelconque des revendications 16 à 32, dans laquelle les monomères à insaturation éthylénique de la composition de monomères A sont tels que définis dans l'une quelconque des revendications 7 et 8.
34. Composition thermodurcissable comprenant une phase résineuse dispersée dans un milieu aqueux, ladite phase résineuse comprenant les composants suivants :

(a) un copolymère non statistique non gélifié de formule générale suivante :



dans laquelle :

- (1) A et B sont des compositions différentes de monomères à insaturation éthylénique, B contenant des monomères fonctionnels ayant un groupe fonctionnel choisi dans l'ensemble constitué par les groupes hydrogène actif et les groupes sel d'onium ;
- (2) p est un entier de 1 à 1000 ;
- (3) s est un entier de 1 à 1000 ;
- (4) t est un entier de 1 à 100 ; et
- (5) ϕ est un résidu provenant d'un radical centré sur un carbone capable d'amorcer une polymérisation radicalaire ; et

(b) un agent durcisseur ayant au moins deux groupes fonctionnels qui sont réactifs avec les groupes hydrogène actif de (a).

35. Composition thermodurcissable selon la revendication 34, dans laquelle le polymère contenant des groupes hydrogène actif a une masse moléculaire moyenne en nombre située dans la plage allant de 1 000 à 30 000.

36. Composition thermodurcissable selon la revendication 34, dans laquelle le polymère a une masse équivalente de groupes sel d'onium de 1 000 à 15 000 grammes/équivalent.
- 5 37. Composition thermodurcissable selon la revendication 34, dans laquelle A est un résidu dérivant d'au moins l'un parmi les monomères de vinyle, les monomères allyliques, et les oléfines.
- 10 38. Composition thermodurcissable selon la revendication 34, dans laquelle A dérive d'au moins l'un parmi les (méth)acrylates d'alkyle ayant de 1 à 20 atomes de carbone dans le groupe alkyle, les monomères vinylaromatiques et les oléfines.
- 15 39. Composition thermodurcissable selon la revendication 34, dans laquelle les groupes hydrogène actif de la composition de monomères B dérivent d'au moins l'un parmi les esters hydroxyalkyliques d'acide (méth)acrylique contenant de 1 à 4 atomes de carbone dans le groupe hydroxyalkyle.
- 20 40. Composition thermodurcissable selon la revendication 34, dans laquelle les groupes hydrogène actif de la composition de monomères B dérivent d'au moins l'un parmi le (méth)acrylate d'hydroxyéthyle et le (méth)acrylate d'hydroxypropyle.
- 25 41. Composition thermodurcissable selon la revendication 34, dans laquelle le sel d'onium de la composition de monomères B est choisi parmi au moins l'un de la classe constituée des sels d'ammonium quaternaire et des sels de sulfonium quaternaire.
- 30 42. Composition thermodurcissable selon la revendication 34, dans laquelle le polymère non aléatoire comprend en outre des segments de composition de monomères G, qui dérive d'au moins un monomère à insaturation éthylénique contenant un groupe époxy qui, après polymérisation, a été soumis à une post-réaction avec un sel d'acide aminé.
- 35 43. Composition thermodurcissable selon la revendication 42, dans laquelle G dérive d'au moins un monomère contenant un groupe époxy qui, après polymérisation, a été soumis à une post-réaction avec un sel d'acide aminé ;
B dérive d'au moins un (méth)acrylate d'hydroxyalkyle ayant de 1 à 4 atomes de carbone dans le groupe alkyle ; et
A dérive d'au moins l'un parmi les monomères (méth)acrylates, les monomères vinylaromatiques, et les oléfines.
- 40 44. Composition thermodurcissable selon la revendication 42, dans laquelle le polymère contenant des groupes hydrogène actif est un polymère pratiquement linéaire ayant une masse moléculaire moyenne en nombre située dans la plage allant de 1 000 à 30 000, et dans laquelle
- 45 45. Composition thermodurcissable selon la revendication 44, dans laquelle le polymère a une masse équivalente de groupes sel d'onium située dans la plage allant de 1 000 à 15 000 grammes/équivalent.
- 50 46. Composition thermodurcissable selon la revendication 44, dans laquelle le polymère, avant la formation des groupes sel d'onium, a un indice de polydispersité inférieur à 2,5.
- 55 47. Composition thermodurcissable selon l'une quelconque des revendications 34 à 46, dans laquelle le composant (a) est présent en une quantité située dans la plage allant de 25 à 99 % en poids, et le composant (b) est présent en une quantité située dans la plage allant de 1 à 75 % en poids, les pourcentages en poids étant basés sur le poids total de (a) et (b).
48. Composition thermodurcissable selon l'une quelconque des revendications 16 à 47, dans laquelle le résidu ϕ est tel que défini dans l'une quelconque des revendications 10 à 12.

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